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MASTER'S THESIS IN PHYSICS

FREQUENCY-DEPENDENT MAGNETIZABILITY

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Contents

Introduction

The purpose of this work is to analyze in detail a specific second-order magnetic property, namely the leading-order interaction between a molecule and an external magnetic field, commonly named the magnetizability of a molecule. The reason why we are interested in studying this property is because the expression obtained using the standard multipole approach is origin dependent when an external frequency-dependent magnetic field is applied[1]. This result appears surprising given that, when considering an external static magnetic field, the magnetizability should be an observable quantity and its expression is actually origin-independent, so we would expect to have an origin independent expression also in the frequency-dependent case. In particular, I will focus on discussing the frequency-dependent magnetizability in a relativistic framework.
Several approaches have been used to analyse molecular properties in relativistic and non-relativistic frameworks. I will describe the most important ones and then reduce the analysis to the multipole theory that so far has been the most successful way to study molecular properties for closed-shell molecules.
I will start by giving an overview of electrodynamics and by explaining the theoretical aspects that lead us to consider a particular form of the Hamiltonian, a crucial point in the definition of molecular properties. The differences between the relativistic and the non-relativistic framework will also be underlined, in order to identify the best way to treat the invariance problem.
Particular attention will be paid to the gauge issue. It is well known from electrodynamics that the presence of a magnetic field involve a non-unique definition of the vector and scalar potentials, and therefore a freedom in the choice of gauge. In the literature, several gauges have been used[2], but here I will focus on the multipole gauge[3],[4] in the derivation of the expressions of molecular properties. I will also analyze the problem of gauge origin with respect to the problem of origin dependence of an observable, and discuss the different aspects of each issue.
A wide analysis of the origin-dependence of the magnetizability within the

non-relativistic framework will be done, including a review of the results obtained by Van Vleck[5], and Raab and de Lange[6] regarding the origin independence of the magnetizability in the static and frequency-dependent case, respectively. Special emphasis will be given to the works of the latter, discussing their proposal of an origin-independent expression for the frequency-dependent magnetizability.

The magnetizability will also be discussed within a relativistic framework, where its expression looks different from the non-relativistic one, given the absence of second-order terms in the vector potential in the relativistic Hamiltonian. The relativistic formulation of the description of the magnetizability may prove a very good starting point, considering that the Maxwell equations are fully relativistic.

Extending the discussion to the macroscopic electrodynamics, we will observe that the multipole description leads to origin-dependent expressions of the material constants, written as linear combinations of polarizabilities of various multipole orders. Despite this, the macroscopic Maxwell equations do not define the response fields uniquely, therefore it will be possible transform the fields leaving the Maxwell equations unchanged; in this way I will obtain, by construction, origin-independent expressions of the material constants[7],[8].

Origin-independent expressions of the material constants will be discussed, trying to extend the same analysis to the microscopic case and to understand why multipole theory does not give physical acceptable results, but it is necessary transform the response fields.

Finally, I will introduce other possible approaches to study the problem of origin dependence of the magnetizability, and I will consider calculation of static and dynamic second-order magnetic response.

Before discussing each of these different points in detail, I would like to point out a possible misunderstanding about the terminology used. The second-order magnetic response of a system is usually named magnetizability. Non-relativistic static expression of the magnetizability is the sum of two contributions, paramagnetic and diamagnetic, coming from the linear and quadratic term in the vector potential of the non-relativistic Hamiltonian. The relativistic Hamiltonian has no quadratic term in the vector potential, therefore the expression of the static magnetizability has only the paramagnetic term[9].

When the frequency-dependent case is considered, the magnetizability turns out to be an origin-dependent quantity, thus it cannot be an observable anymore. An origin-independent expression has been obtained as a sum of different polarizabilities, in such a way that the frequency-dependent magnetizability does not contain only the paramagnetic and diamagnetic terms anymore. In view of this, it will be more appropriate to call the frequency-dependent magnetizability a second-order magnetic response instead, and leave the name magnetizability to the expression formed by the paramagnetic and diamagnetic terms only. From now I will use this terminology.

Chapter 1

Electromagnetism and the gauge invariance

The complete theory that describes the interactions of molecules with external fields is given by QED, where both the molecules and the fields are quantized. However, it is common use a semi-classical approach and consider continuous fields, whose dynamics is defined by the Maxwell equations[2]:

$$\nabla \cdot \boldsymbol{B} = 0 \tag{1.1}$$

$$\nabla \wedge \boldsymbol{E} + \frac{\partial \boldsymbol{B}}{\partial t} = 0 \tag{1.2}$$

$$\nabla \cdot \boldsymbol{E} = \frac{\rho}{\varepsilon_0} \tag{1.3}$$

$$\nabla \wedge \boldsymbol{B} - \mu_0 \varepsilon_0 \frac{\partial \boldsymbol{E}}{\partial t} = \mu_0 \boldsymbol{j} \tag{1.4}$$

Thus we have a system of six coupled first-order differential equations for the components of the fields $\boldsymbol{E}$ and $\boldsymbol{B}$. The first two equations are known as the homogeneous Maxwell equations, while the last two as the inhomogeneous Maxwell equations, where in the right-hand side we can recognize the charge density ρ and the current density $\boldsymbol{j}$. Here, I am considering the microscopic Maxwell equations in the SI units, where ε_0 is the permittivity and μ_0 is the permeability of the free space; these two constants are related by: $\varepsilon_0 \mu_0 = \frac{1}{c^2}$. Using the inhomogeneous equations and taking the divergence of Ampere's law (1.4), an important relation can be derived, namely the continuity equation:

$$\nabla \cdot \boldsymbol{j} + \frac{\partial \rho}{\partial t} = 0 \tag{1.5}$$

which define the conservation of the charges in a system, and extend the validity of Ampere's law to the case of time-dependent fields, suggesting the existence of electromagnetic waves. The Maxwell equations form the basis of all electromagnetic phenomena, and when combined with the Lorentz force and Newton's second law of motion they provide a complete description of the classical interaction between charged particles and electromagnetic fields.
A generalization to the macroscopic case of the microscopic Maxwell equations, taking in account the nature of the materials, can be done, and will be considered later in this work.
In the description of electromagnetic fields, a central role is played by the scalar potential ϕ and by the vector potential $\boldsymbol{A}$, in terms of which the Maxwell equations are usually rewritten. In fact, exploiting Helmholtz theorem[10], it is possible define the magnetic fields as:

$$\boldsymbol{B} = \nabla \wedge \boldsymbol{A} \tag{1.6}$$

and the electric field as:

$$\boldsymbol{E} = -\nabla\phi - \frac{\partial \boldsymbol{A}}{\partial t} \tag{1.7}$$

Inserting these definitions into the inhomogeneous Maxwell equations, we can see that the scalar and the vector potential, respectively, satisfy the second-order differential equations:

$$\nabla^2\phi + \frac{\partial}{\partial t}(\nabla \cdot \boldsymbol{A}) = -\frac{\rho}{\varepsilon_0} \tag{1.8}$$

$$\nabla^2\boldsymbol{A} - \mu_0\varepsilon_0\frac{\partial^2 \boldsymbol{A}}{\partial t^2} - \nabla(\nabla \cdot \boldsymbol{A} + \mu_0\varepsilon_0\frac{\partial\phi}{\partial t}) = -\mu_0\boldsymbol{j} \tag{1.9}$$

which have the form of wave equations, and thus indicates the existence of electromagnetic waves.
Introducing the electromagnetic potentials is fundamental in the description of electrodynamics, despite the fact they are not uniquely defined until an explicit choice of gauge is made. In fact, by definition of $\boldsymbol{B}$ in terms of the vector potential, we could freely add to $\boldsymbol{A}$ the gradient of some scalar function Λ, without affect the magnetic field:

$$\boldsymbol{A}' = \boldsymbol{A} + \nabla\Lambda \tag{1.10}$$

In the same way, from equation (1.7), the scalar potential can be modified adding the time derivative of a scalar function, and leaving the electric field unchanged:

$$\phi' = \phi - \frac{\partial\Lambda}{\partial t} \tag{1.11}$$

The last two equations are known in the literature as gauge transformations[2], and they leave the fields unchanged (gauge invariance). Note that, since the scalar and the vector potentials are related through equation (1.7), a modification of the scalar (vector) potential imply a modification of the vector (scalar) potential, in order to leave the electric field unchanged; therefore the gauge transformations (1.10) and (1.11) have to be applied simultaneously. The gauge freedom can be exploited to decouple the vector and the scalar potentials in the inhomogeneous equations (1.8) and (1.9), choosing a set of potentials that satisfy the condition:

$$\nabla \cdot \boldsymbol{A} + \frac{1}{c^2}\frac{\partial \phi}{\partial t} = 0 \tag{1.12}$$

Therefore we obtain the two wave equations:

$$\nabla^2 \phi - \frac{1}{c^2}\frac{\partial^2 \phi}{\partial t^2} = -\frac{\rho}{\varepsilon_0} \tag{1.13}$$

$$\nabla^2 \boldsymbol{A} - \frac{1}{c^2}\frac{\partial^2 \boldsymbol{A}}{\partial t^2} = -\mu_0 \boldsymbol{j} \tag{1.14}$$

totally equivalent to the Maxwell equations. Equation (1.12) represents a particular choice of gauge, known as the Lorentz gauge. More precisely it defines a class of gauges, where a specific gauge is completely defined by choosing a function Λ that satisfy the wave equation:

$$\nabla^2 \Lambda - \frac{1}{c^2}\frac{\partial^2 \Lambda}{\partial t^2} = 0 \tag{1.15}$$

A fundamental feature of the Maxwell equations is that they are fully relativistic[11], therefore it comes natural to use the Lorentz gauge, given that it does not depend on the choice of the coordinate system, and so it perfectly match with the concepts of special relativity. Furthermore, general solutions of the wave equations (1.13) and (1.14) are the retarded potentials, which take into account the finite time of propagation of the fields predicted by the relativistic theory. In terms of the four-vector potential $A_\alpha = (\boldsymbol{A}, \frac{i}{c}\phi)$ and using covariant notation[11], we can rewrite the Lorentz gauge as $\partial_\alpha A_\alpha = 0$, where $\partial_\alpha = (\nabla, -\frac{i}{c}\frac{\partial}{\partial t})$.

An infinite number of choices of gauge are possible. One of the most common gauge that has been used in literature is the Coulomb gauge:

$$\nabla \cdot \boldsymbol{A} = 0 \tag{1.16}$$

The Coulomb gauge implies the separation of the static and dynamic aspects of the source of the electromagnetic fields, and leads to the Poisson equation for the scalar potential:

$$\nabla^2\phi = -\frac{\rho}{\varepsilon_0} \tag{1.17}$$

Solution of the Poisson equation is the instantaneous Coulomb potential given by the charge density ρ, still the Coulomb gauge it is often used also when no sources are present[1]. Furthermore, exploiting the Helmholtz theorem, this gauge allows us to express the wave equation for the vector potential only in terms of the transversal part of the current density. Obviously the Coulomb gauge it is not the best choice within a relativistic framework, given that it leads to an instantaneous scalar potential, equivalent to the results obtained in static electromagnetism, and in contrast to the principles of special relativity.
It is worth to note that neither the Coulomb gauge nor the Lorentz gauge completely fix the electromagnetic potentials. In particular, the Coulomb gauge is preserved when the gauge function Λ satisfy the Laplace equation $\nabla^2\Lambda = 0$, whereas the Lorentz gauge is preserved when Λ satisfy the wave equation $\nabla^2\Lambda - \frac{1}{c^2}\frac{\partial^2\Lambda}{\partial t^2} = 0$. In the static limit, the two gauges are equivalents.
In this work I will rather choose another gauge, which is commonly known as the multipole gauge[3], although in the literature several names have been used for it, e.g.Barron-Gray gauge[1]. The main idea of the multipole gauge is to expand the vector and the scalar potentials in a power series, so that, through equations (1.6) and (1.7), a Taylor expansion of the electric and magnetic fields is obtained. Considering a Taylor expansion of the external fields is definitely reasonable, in fact they are much weaker than the internal fields of a molecule, and their effects on a system are commonly studied using perturbation theory. The multipole gauge allow us to rewrite the vector and the scalar potentials directly in terms of the electric and magnetic fields, and thus define their expansion as a series of multipole moments. This fact turns out to be a fundamental feature of the multipole gauge in order to study molecular properties, which are often defined through the expectation value of multipole moments[1].
Let start considering a Taylor expansion of the scalar potential, and rewrite it in terms of the electric field and of the vector potential, using the rela-

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[1] We will see in the next section that the use of the Coulomb gauge simplify the expression of the non-relativistic Hamiltonian that describes the interaction between atoms and electromagnetic fields.

tion (1.7):

$$\begin{aligned}\phi(\boldsymbol{r},t) &= \phi(\boldsymbol{0},t) - E_i(0,t)r_i - \frac{1}{2}[\nabla_j E_i(\boldsymbol{r},t)]r_i r_j - \dots \\ &\quad - r_i\frac{\partial A_i(0,t)}{\partial t} - \frac{1}{2}r_i r_j\frac{\partial}{\partial t}\nabla_j A_i(\boldsymbol{r},t) - \dots\end{aligned}\tag{1.18}$$

This equation can be written as:

$$\phi(\boldsymbol{r},t) = \phi'(\boldsymbol{r},t) - \frac{\partial\Lambda}{\partial t}\tag{1.19}$$

where Λ is the gauge function:

$$\Lambda = \sum_{n=0}^{\infty}\frac{1}{(n+1)!}\{\boldsymbol{r}\cdot\boldsymbol{A}^{[n]}_{j_1\dots j_n}\}r_{j_1}\dots r_{j_n}\tag{1.20}$$

Inserting the definition of the gauge function in the gauge transformations (1.10) and (1.11), the expression of the vector and of the scalar potential in the multipole gauge can be derived as:

$$\begin{aligned}A_i(\boldsymbol{r},t) &= \varepsilon_{ijk}\{\frac{1}{2}B_j(0,t)r_k + \frac{1}{3}[\nabla_\ell B_j(\boldsymbol{r},t)]r_k r_\ell \\ &\quad + \frac{1}{8}[\nabla_m\nabla_\ell B_j(\boldsymbol{r},t)]r_k r_\ell r_m + \dots\}\end{aligned}\tag{1.21}$$

$$\begin{aligned}\phi(\boldsymbol{r},t) &= \phi(\boldsymbol{0},t) - E_i(0,t)r_i - \frac{1}{2}[\nabla_j E_i(\boldsymbol{r},t)]r_i r_j \\ &\quad - \frac{1}{6}[\nabla_k\nabla_j E_i(\boldsymbol{r},t)]r_i r_j r_k + \dots\end{aligned}\tag{1.22}$$

where I have used the Einstein notation that implies implicit summation over repeated indices. Using equations (1.6) and (1.7), we obtain Taylor expansions of the fields:

$$E_i(\boldsymbol{r},t) = E_i(0,t) + [\nabla_j E_i(\boldsymbol{r},t)]r_j + \frac{1}{2}[\nabla_k\nabla_j E_i(\boldsymbol{r},t)]r_j r_k + \dots\tag{1.23}$$

$$B_i(\boldsymbol{r},t) = B_i(0,t) + [\nabla_j B_i(\boldsymbol{r},t)]r_j + \frac{1}{2}[\nabla_k\nabla_j B_i(\boldsymbol{r},t)]r_j r_k + \dots\tag{1.24}$$

It is worth to note that the choice of $\boldsymbol{A}$ and ϕ is unique and determined by the Maxwell equations, and the condition for the multipole gauge can be written as: $\boldsymbol{r}\cdot\boldsymbol{A} = 0$. Furthermore, from equations (1.21) and (1.22), the standard forms of the static homogeneous electric ($\boldsymbol{A} = 0$) and magnetic ($\phi = 0$) fields are respectively recovered, considering only the first-order terms of the expansions.

Important aspects of the gauge issue can be analysed within the formalism of quantum mechanics[12]. Since the formalism of quantum mechanics is invariant under unitary transformations of wave functions, it is possible have invariance to particular transformations if they can be reduced to unitary transformations. A gauge transformation of the vector potential (1.10) imply a transformation of the wave function[13][2]:

$$\Psi(\boldsymbol{A}', t) = e^{-\imath\Lambda(t)}\Psi(\boldsymbol{A}, t) \tag{1.25}$$

and correspondingly of the Hamiltonian:

$$H(\boldsymbol{A}', t) = e^{-\imath\Lambda(t)}H(\boldsymbol{A}, t)e^{\imath\Lambda(t)} - \imath e^{-\imath\Lambda(t)}\frac{\partial\Lambda(t)}{\partial t}e^{\imath\Lambda(t)} \tag{1.26}$$

In this case Λ is a collection of real functions that specify the gauge transformation:

$$\Lambda(t) = \frac{1}{c}\sum_{i=1}^{N}\sum_{\alpha}\epsilon_\alpha\lambda_\alpha(r_i, t) \tag{1.27}$$

Equation (1.26) can be expanded as:

$$H(\boldsymbol{A}', t) = H(\boldsymbol{A}, t) - \imath[\Lambda(t), H(\boldsymbol{A}, t)] + \cdots \tag{1.28}$$

Using perturbation theory, the first-order change in the energy turns out to be:

$$E^{(1)} = -\imath < \Psi(\boldsymbol{A}, t) \mid [\Lambda(t), H(\boldsymbol{A}, t)] \mid \Psi(\boldsymbol{A}, t) > \tag{1.29}$$

Here I have introduced the most general gauge transformation, which is not a unitary transformation. However, considering the particular case of a unitary transformation, it is possible to derive an important theorem. In fact, since the energy is gauge invariant under a unitary transformation, the first order perturbation in the energy $E^{(1)}$ vanish. Thus gauge invariance lead to the well known hypervirial theorem[14]:

$$< \Psi(\boldsymbol{A}, t) \mid [\Lambda(t), H(\boldsymbol{A}, t)] \mid \Psi(\boldsymbol{A}, t) >= 0 \tag{1.30}$$

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[2] We are considering eigenstate Ψ of a non-relativistic Hamiltonian that describe a molecular system in an external magnetic field.

The hypervirial theorem is obviously valid for a complete set of eigenfunctions, or if the set of eigenfunctions is invariant to the set of gauge transformation $e^{-\imath\Lambda(t)}$, and it has been used to prove the origin-independence of the frequency-independent magnetizability[3]. Furthermore, integrating by parts equation (1.30), we have:

$$\int d\boldsymbol{r}\nabla\cdot\boldsymbol{j}\lambda_{\alpha}=0\Longrightarrow\nabla\cdot\boldsymbol{j}=0 \tag{1.31}$$

so gauge invariance also imply current conservation.

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[3] See chapter 3.

Chapter 2

Lagrangians and Hamiltonians

In this chapter I will discuss the theoretical approach used to analyze the interaction of a molecule with external fields. I will start describing the interaction of a charged particle with electromagnetic fields using the Lagrangian formalism, and from it I will derive the relativistic and non-relativistic Hamiltonians for such a system. I will also derive the expressions for the current and the charge density in both cases, and I will point out the different results coming from the possible choices of gauge. As already mentioned, my focus will be on the multipole gauge that allows us to express the Hamiltonians as an expansion of multipole moments[1]. The following discussion represents the theoretical basis to introduce and define molecular properties, and it constitute the framework for all the further analysis.

2.1 The Lagrangian formalism

Let us define the Lagrangian: the Lagrangian of a dynamical system is a function that summarizes the dynamics of the system. In classical mechanics, the Lagrangian is defined as the kinetic energy T of the system minus its potential energy U: $L = T - U$, where U depends only on the position. Under conditions that are given in Lagrangian mechanics, if the Lagrangian of a system is known, then the equations of motion of the system may be obtained by a direct substitution of it into the Euler-Lagrange equation[15]. Although the Lagrangian formalism has been created to describe classical mechanics, and therefore to treat continuous quantities[2], the action principle that is

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[1] In the next sections multipole moments will be discussed in details.

[2] Usually a classical system is described by a Lagrangian density. Integration on the continuous variables of the system give the Lagrangian of the system.

used to derive the Lagrange equation, is now recognized as being applicable to quantum mechanics. Lagrangian mechanics and Noether's theorem, which relates physical conserved quantities to continuous symmetries of a physical system together, yield a natural formalism for first quantization[17].
The Lagrangian density that describe a charged particle in the presence of an external electromagnetic field, using the covariant notation, has the form[18]:

$$\mathfrak{L} = \mathfrak{L}_m + \mathfrak{L}_f + \mathfrak{L}_{mf} = -mc^2\gamma^{-1} - \frac{1}{4\mu_0}F_{\alpha\beta}F^{\alpha\beta} + j_\alpha A_\alpha \tag{2.1}$$

where the first term is the Lagrangian density of a free particle, the second is the Lagrangian density of the free field, and the third is the Lagrangian of the interaction between the charged particle and the external field. Note that in this equation m is the mass of the particle, $\gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$ is the relativistic Lorentz factor, and $F^{\alpha\beta}$ is the antisymmetric electromagnetic tensor. Following a semiclassical approach, it is possible consider the external field as fixed and neglect the second term in equation (2.1). This form obey the requirement of Lorentz invariance, and under a gauge transformation the interaction term is modified as:

$$\mathfrak{L}'_{mf} = \mathfrak{L}_{mf} + \partial_\alpha(j_\alpha\Lambda) - \Lambda\partial_\alpha j_\alpha \tag{2.2}$$

The first term gives zero upon integration due to the boundary conditions, while the second term is zero according to the continuity equation. This result shows that there is an intimate connection between gauge invariance and charge conservation.
By integration, and using the definition of the charge density $\rho(\boldsymbol{r}) = q\delta^3(\boldsymbol{r'} - \boldsymbol{r}(t))$[3], the Lagrangian assume the form:

$$L = -mc^2\gamma^{-1} + \boldsymbol{j}\cdot\boldsymbol{A} - q\phi \tag{2.3}$$

Note that using the principle of least action and substituting this Lagrangian in the Euler-Lagrange equation, the Maxwell equations and the Lorentz force can be derived[19].

2.2 The relativistic Hamiltonian

A physical system is often described through its Hamiltonian. The Hamiltonian method differs from the Lagrangian method in that instead of expressing second-order differential constraints on an n-dimensional coordinate

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[3] Use the definition of the charge density in the integration of the Lagrangian density imply the loss of the covariant formalism.

space (where n is the number of degrees of freedom of the system), it expresses first-order constraints on a 2n-dimensional phase space. Generally, the Hamiltonian formalism does not provide a more convenient way of solving a particular problem, rather it provides deeper insights into both the general structure of classical mechanics and its connection to quantum mechanics. It is possible to move from the Lagrangian of a system to its Hamiltonian using the Legendre transformation[20]. Thus, the Hamiltonian for a free particle is:

$$H = c\sqrt{m^2c^2 + p^2} \tag{2.4}$$

and, from equation (2.3), the Hamiltonian of a charged particle in an external electromagnetic field is:

$$H = c\sqrt{m^2c^2 + \pi^2} + e\phi \tag{2.5}$$

By comparison, the latter equation, which include the electromagnetic interaction, can be inferred from the Hamiltonian of a free particle through the minimal substitution[21]:

$$\boldsymbol{p} \longrightarrow \boldsymbol{\pi} = \boldsymbol{p} + e\boldsymbol{A} \quad , \quad H \longrightarrow H + e\phi \tag{2.6}$$

where $\boldsymbol{\pi}$ is the mechanical momentum and $\boldsymbol{p}$ is the conjugate momentum. Note that the minimal coupling imply a specific choice of the charge, in our case I have considered the electron's charge $q = -e$.

So far, I have been working in a classical framework, without consider any quantization of the physical systems. Let now consider the quantum mechanical expression of the Hamiltonian. A standard approach to move from the classical to the quantum theory is to associate to each physical observable a linear operator. Inserting the momentum operator in equation (2.5) and taking the square of it, we obtain the Klein-Gordon equation[22]:

$$(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 + \frac{m^2c^2}{\hbar^2})\psi = 0 \tag{2.7}$$

The Klein-Gordon equation is the relativistic field equation for a scalar particle (spin=0), but it does not correctly describe the behavior of a half-spin particle (spin=$\frac{1}{2}$). Thus, in order to analyze an electronic system in the presence of an electromagnetic field, it is necessary to use the Dirac equation[23]. To simplify things, let us consider the Dirac equation for a one-electron system, derived from the Dirac equation for a free particle[4] through the minimal substitution:

$$H_D = \beta mc^2 + c(\boldsymbol{\alpha} \cdot \boldsymbol{p}) + ec(\boldsymbol{\alpha} \cdot \boldsymbol{A}) - e\phi \tag{2.8}$$

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[4] $H_D = \beta mc^2 + c(\boldsymbol{\alpha} \cdot \boldsymbol{p})$.

Here $\boldsymbol{\alpha}$ and β are the 4x4 Dirac matrices defined as:

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma}_2 \\ \boldsymbol{\sigma}_2 & 0 \end{pmatrix} \tag{2.9}$$

$$\beta = \begin{pmatrix} \mathbf{1}_2 & 0 \\ 0 & -\mathbf{1}_2 \end{pmatrix} \tag{2.10}$$

where $\boldsymbol{\sigma}$ are the Pauli's matrices[27]. Note that a solution of the Dirac equation is a 4-component wave function (4-spinors), and (for a spin-one-half particle) it is automatically a solution of the Klein-Gordon equation, though not all solutions of the Klein-Gordon equation are solutions of the Dirac equation.

The expectation value of the Dirac operator give the energy of the system. Considering the terms that involve the external potentials, and the previous definition of the Lagrangian, the expressions of the relativistic charge and current density can be derived:

$$E_{mf} = < \psi| - e\phi + ec(\boldsymbol{\sigma} \cdot \boldsymbol{A})|\psi > = \int \phi(\boldsymbol{r})\rho(\boldsymbol{r})d\tau - \int \boldsymbol{A}(\boldsymbol{r}) \cdot \boldsymbol{j}(\boldsymbol{r})d\tau \tag{2.11}$$

$$\rho = -e\psi^\dagger\psi \quad \boldsymbol{j} = -e\psi^\dagger c\boldsymbol{\alpha}\psi \tag{2.12}$$

The Dirac equation will play a central role in my work, given that it will be the starting point for studying the magnetizability in both the non-relativistic and the relativistic framework.

2.3 The non-relativistic Hamiltonian

Let us now derive the non-relativistic Hamiltonian from the Dirac equation. At first the matrix β is replaced by the matrix $\beta' = \beta - mc^2$ in order to align the energy level of the relativistic and the non-relativistic case. It is not possible to take directly the non-relativistic limit ($c \to \infty$) of the Dirac equation, because it contains terms linear and quadratic in c, therefore it is necessary to operate a change of metric. Reducing the description to only positive-energy solutions and solving for the small components of the wave equation, the non-relativistic limit of the Dirac equation is[16]:

$$H_{NR} = \frac{1}{2m}(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})(\boldsymbol{\sigma} \cdot \boldsymbol{\pi}) - e\phi \tag{2.13}$$

By definition of the mechanical momentum $\boldsymbol{\pi}$ and through easy manipulation of the previous equation, the non-relativistic Hamiltonian for a free particle and in the presence of an external electromagnetic field are respectively:

$$H_{NR} = \frac{p^2}{2m} \tag{2.14}$$

$$H_{NR} = \frac{p^2}{2m} + \frac{e}{2m}(\boldsymbol{A}\cdot\boldsymbol{p} + \boldsymbol{p}\cdot\boldsymbol{A}) + \frac{e}{2m}(\boldsymbol{B}\cdot\boldsymbol{\sigma}) - e\phi \tag{2.15}$$

These equations, obtained as the non-relativistic limit of the Dirac equation, perfectly match with the well-known Schrödinger equation[24], and show that the spin is not a pure relativistic effect, but it is already present inside the term p^2. Note that the Zeeman term in the expression of the non-relativistic Hamiltonian define the interaction between an external magnetic field and the spin of the electron, and it comes naturally substituting $\boldsymbol{p}$ with $(\boldsymbol{\sigma}\cdot\boldsymbol{p})$ in the field-free Hamiltonian. This term is usually multiplied by the gyro electric factor $g_e \simeq 2$ given by QED.
Following the same procedure for the relativistic case, the non-relativistic expressions of the charge and current densities are:

$$\rho = -e\psi^\dagger_{NR}\psi_{NR} \tag{2.16}$$

$$\begin{aligned} \boldsymbol{j}_{NR} \;=\; & -\frac{e}{2m}\{\psi^\dagger_{NR}\boldsymbol{p}\psi_{NR} - \psi^T_{NR}\boldsymbol{p}\psi^*_{NR}\} - \frac{e}{2m}\{\psi^\dagger_{NR}\boldsymbol{A}\psi_{NR}\} \\ & - \frac{e}{2m}\nabla\wedge\{\psi^\dagger_{NR}\boldsymbol{\sigma}\psi_{NR}\} \end{aligned} \tag{2.17}$$

The latter expression requires a few manipulations and integration by parts, in order to be written in this form. The first term in equation (2.17) is the contribution given by the motion of the electrons, the second describe the current induced by the vector potential (Larmor current), the third is a pure transversal quantity that comes from the electron spin. A comparison with equation (2.12) shows that the non-relativistic expression of the charge density is similar to the one obtained from the relativistic Hamiltonian, instead a much more cumbersome expression of the current density is derived in the non-relativistic case. Thus, it becomes natural to ask why the expression of the non-relativistic current density is so different from the relativistic one. The analysis of this issue is important, in order to discuss a fundamental point of electromagnetic theory: the relativistic character of the Maxwell equations. In fact, the Maxwell equations obey to the Lorentz transformation, and are so purely relativistic. When the non-relativistic limit of the Dirac Hamiltonian is discussed, a correct analysis should consider the non-relativistic limit of the Maxwell equations too, in order to avoid inconsistencies in the theory and cumbersome expressions as the one given in eq. (2.17). Relevant problems emerge when the non-relativistic limit of the Maxwell equations is considered: the speed of light appear differently depending on the unit system used; the electrostatic laws are recovered, thus no magnetic field (no vector potential $\boldsymbol{A}$) can exist, and therefore no gauge freedom. In SI units, used so far, the speed of light is expressed by the electric permittivity ε_0 and the magnetic permeability μ_0 through the relation: $c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}$. Considering either ε_0 or μ_0 in the non-relativistic limit of the Maxwell equation leads to the electrostatic or to the magnetostatic, respectively. Anyway, the vector potential goes to zero in both cases, therefore the existence of magnetic fields could be considered as a purely relativistic effect. Only the instantaneous Coulomb potential emerge in the non-relativistic limit, and no retardation effects appear. When the interaction between atomic systems and external fields is dominated by the Coulomb potential, the non-relativistic framework is suitable and it describes some phenomena well. However, a complete analysis of a system has to be done using the Dirac Hamiltonian, but the price to pay is the need to consider a 4-component wave vector and a much more complex formalism.

Chapter 3

Molecular properties and the magnetizability in a non-relativistic framework

In this chapter I will analyse molecular properties using a non-relativistic approach, and in particular I will focus my attention on the magnetizability. The problem of origin dependence of the magnetizability will be discuss in detail, considering the different cases of static and dynamic external magnetic fields. I will show that in the former case the expression of the magnetizability given by multipole theory is origin independent for a complete variational basis set, whereas in the latter case multipole theory provides an origin-dependent expression of this property. The origin-independent expression of the frequency-dependent magnetizability proposed by Raab and de Lange will be derived and discussed, pointing out the weak points of their theoretical analysis and introducing other possible approaches.

3.1 A theoretical approach to study molecular properties

Magnetic properties can be defined in several ways. My analysis started from the non-relativistic framework, paying particular attention to the magnetizability, and referring to the theory developed by Raab and de Lange[1],[8]. I focused my attention on this particular approach, because it turned out to be very useful in order to describe time-dependent external perturbations, and in particular to derive an origin-independent expression of the frequency-dependent magnetizability. This expression has been derived by the same (quoted) authors[6],[8]. The crucial point of their theory is the power series expansion of the vector potential and of the scalar potential (multipole gauge), generated by the external fields, that leads to a multipole expansion of the Hamiltonian, and to general expressions for the electric and magnetic multipole moments up to the electric octopole-magnetic quadrupole order. We will observe that the truncation at the above mentioned order will be good enough to derive an origin-independent expression for the frequency-dependent magnetizability.

Let us start by considering the non-relativistic Hamiltonian derived in the previous section:

$$H = H_0 + H_1 + H_2 \tag{3.1}$$

where

$$H_0 = \frac{p^2}{2m} + V \ ; \ H_1 = \frac{e}{2m}(\boldsymbol{p} \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \boldsymbol{p}) - e\phi \ ; \ H_2 = \frac{e^2}{2m} A^2 \tag{3.2}$$

and V is the potential energy operator in the absence of the fields. The choice of a certain gauge will appear very important in treating the magnetizability, so it is wise to approach the analysis of this property starting with the Hamiltonian just considered in equation (3.1), where no restriction to any particular gauge is done yet. In H, the nuclear magnetic moments have not been considered, so that all the interaction terms deriving from their presence have been ignored. Furthermore, I have assumed to work with closed-shell molecules, and therefore the spin-dependent part given by the interaction of the external magnetic field with the intrinsic magnetic moment can be neglected.

In general, quantum-mechanical expressions for the electrodynamic polarizability tensors are derived from the expectation value of the appropriate multipole moment operator. Therefore, when considering time-dependent external perturbations, it is natural to switch to time-dependent perturbation theory in order to derive the correct expression of the perturbed states, and thus to calculate the multipole moment expectation values and the magnetic properties. It is possible to apply perturbation theory and obtain the definitions of the polarizability tensors using this approach, since I refer to weak external perturbations[1]. Furthermore, taking the limit for $\omega = 0$[2], these expressions recover the results that have been obtained in the static case[3].

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[1] This means that the perturbation is much weaker compared with the internal fields of the atoms.

[2] Where ω is the frequency of the applied perturbation.

[3] In the literature the expressions for the polarizabilities are well know and they have been obtained following different approaches, see e.g.Ref.[7].

3.2 The multipole gauge and the polarizabilities

Let us derive the expressions for the polarizabilities, starting with the choice of a particular gauge. Note that, in the method described above, it is common to use the Coulomb gauge: $\nabla\cdot\boldsymbol{A} = 0$. This choice of gauge looks very advantageous referring to the Hamiltonian H_1, but it leads to complicated expressions for the polarizability tensors, that have to be simplified through cumbersome manipulations[1]. In order to reduce the calculations and obtain simpler definitions of frequency dependent properties, it is possible to use the multipole gauge (Barron-Gray gauge). To highlight the reasons for this specific choice, let us observe that we would like to work within multipole theory[4], so it would be nice to get a power expansion of the Hamiltonian, and consequently it is necessary to look at the expansion of the electromagnetic potentials about an origin. Following the Barron-Gray idea, since the electromagnetic potentials are strictly related to the electromagnetic fields[5], then a power series of the potentials should yield a Taylor expansion of the fields. Recalling the definitions of the potentials $\boldsymbol{A}$ and ϕ in the multipole gauge:

$$\begin{aligned} A_\imath(\boldsymbol{r},t) &= \varepsilon_{\imath\jmath k}\{\frac{1}{2}B_\jmath(0,t)r_k + \frac{1}{3}[\nabla_\ell B_\jmath(\boldsymbol{r},t)]r_k r_\ell \\ &\quad + \frac{1}{8}[\nabla_m\nabla_\ell B_\jmath(\boldsymbol{r},t)]r_k r_\ell r_m + \dots\} \end{aligned} \tag{3.3}$$

$$\begin{aligned} \phi(\boldsymbol{r},t) &= \phi(\boldsymbol{0},t) - E_\imath(0,t)r_i - \frac{1}{2}[\nabla_\jmath E_\imath(\boldsymbol{r},t)]r_\imath r_\jmath \\ &\quad - \frac{1}{6}[\nabla_k\nabla_\jmath E_\imath(\boldsymbol{r},t)]r_\imath r_\jmath r_k + \dots \end{aligned} \tag{3.4}$$

the expressions of the fields are obtained through the Maxwell equations. Thus, the Taylor expansion about an origin of arbitrary time-dependent electric and magnetic fields are:

$$E_\imath(\boldsymbol{r},t) = E_\imath(0,t) + [\nabla_\jmath E_\imath(\boldsymbol{r},t)]r_\jmath + \frac{1}{2}[\nabla_k\nabla_\jmath E_\imath(\boldsymbol{r},t)]r_\jmath r_k + \dots \tag{3.5}$$

$$B_\imath(\boldsymbol{r},t) = B_\imath(0,t) + [\nabla_\jmath B_\imath(\boldsymbol{r},t)]r_\jmath + \frac{1}{2}[\nabla_k\nabla_\jmath B_\imath(\boldsymbol{r},t)]r_\jmath r_k + \dots \tag{3.6}$$

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[4] Molecular properties are generally treated within the Response Theory, starting from the Taylor expansion of the potentials and writing multipole expansion of the Hamiltonian.

[5] As a consequence of the Maxwell equations $\boldsymbol{B} = \nabla\wedge\boldsymbol{A}$ and $\boldsymbol{E} = -\nabla\phi - \frac{\partial\boldsymbol{A}}{\partial t}$.

The specific choice of the potentials in eqs. (3.3) and (3.4) defines a particular gauge, namely the multipole/Barron-Gray gauge. These potentials do not satisfy neither the Coulomb gauge

$$\nabla \cdot \boldsymbol{A} = 0 \tag{3.7}$$

nor the Lorentz gauge

$$\nabla \cdot \boldsymbol{A} + \frac{1}{c^2}\frac{\partial \phi}{\partial t} = 0 \tag{3.8}$$

the multipole/Barron-Gray gauge is thus a different possible choice of gauge. Inserting the potentials just defined in the Hamiltonians above and expressing them in terms of $\boldsymbol{E}$ and $\boldsymbol{B}$, it is possible to write:

$$\begin{aligned} H_1 &= q\phi(t) - p_\imath E_\imath(t) - \frac{1}{2}q_{\imath\jmath}E_{\imath\jmath}(t) - \frac{1}{6}q_{\imath\jmath k}E_{\imath\jmath k}(t) - \ldots \\ &\quad - m_\imath B_\imath - \frac{1}{2}m_{\imath\jmath}B_{\imath\jmath}(t) - \frac{1}{6}m_{\imath\jmath k}B_{\imath\jmath k}(t) - \ldots \end{aligned} \tag{3.9}$$

$$\begin{aligned} H_2 &= -\frac{1}{2}\chi_{\imath\jmath}B_\imath(t)B_\jmath(t) - \frac{1}{2}\chi_{\imath\jmath k}B_\imath(t)B_{\jmath k}(t) \\ &\quad - \frac{1}{6}\chi_{\imath\jmath k\ell}B_\imath(t)B_{\jmath k\ell}(t) - \cdots - \frac{4}{27}\chi_{\imath\jmath k\ell}B_{\imath k}(t)B_{\jmath\ell}(t) - \ldots \end{aligned} \tag{3.10}$$

I have here introduced a convenient notation for the fields and for the electric and magnetic multipole moment operators, in order to easily extract the expressions for the polarizabilities. In particular, the fields and their gradients have been defined as:

$$\begin{aligned} E_\imath(t) &= E_\imath(0,t)\ ,\ E_{\imath\jmath}(t) = [\nabla_\jmath E_\imath(\boldsymbol{r},t)]_O, \\ &\quad E_{\imath\jmath k}(t) = [\nabla_k \nabla_\jmath E_\imath(\boldsymbol{r},t)]_O\ ,\ \ldots \end{aligned} \tag{3.11}$$

$$\begin{aligned} B_\imath(t) &= B_\imath(0,t)\ ,\ B_{\imath\jmath}(t) = [\nabla_\jmath B_\imath(\boldsymbol{r},t)]_O, \\ &\quad B_{\imath\jmath k}(t) = [\nabla_k \nabla_\jmath B_\imath(\boldsymbol{r},t)]_O\ ,\ \ldots \end{aligned} \tag{3.12}$$

the electric multipole moment operators as:

$$q = \sum_\alpha q^{(\alpha)}\ ,\ p_\imath = \sum_\alpha q^{(\alpha)} r_\imath^{(\alpha)}\ ,\ q_{\imath,\jmath} = \sum_\alpha q^{(\alpha)} r_\imath^{(\alpha)} r_\jmath^{(\alpha)}\ \ \ldots \tag{3.13}$$

the magnetic multipole moment operators as:

$$m_\imath = \sum_\alpha \frac{q^{(\alpha)}}{2m^{(\alpha)}}\ell_\imath^{(\alpha)}\ ,\ m_{\imath\jmath} = \sum_\alpha \frac{q^{(\alpha)}}{3m^{(\alpha)}}(r_\jmath^{(\alpha)}\ell_\imath^{(\alpha)} + \ell_\imath^{(\alpha)} r_\jmath^{(\alpha)})\ ,\ \ldots \tag{3.14}$$

and the diamagnetic part of the magnetizability operator[6], or magnetic susceptibility, as:

$$\chi_{\imath\jmath} = \sum_{\alpha} \frac{(q^{(\alpha)})^2}{4m^{(\alpha)}} (r_{\imath}^{(\alpha)} r_{\jmath}^{(\alpha)} - (r^{(\alpha)})^2 \delta_{\imath\jmath}) \ , \ \ldots \tag{3.15}$$

where $q^{(\alpha)}$ is the electronic charge, $m^{(\alpha)}$ is the electronic mass, $l^{(\alpha)}$ is the angular momentum operator and the index α runs over all the electrons of the system. I explicitly wrote down only the terms that have been of interest in my work.

It is important to note that the above operators are Hermitian. This observation allow us to simplify several calculations, and it is a useful constraint in order to derive an origin-independent expression for the magnetizability.

At this point we have all the assumptions needed to compute the expectation value of the multipole moment operators in the presence of a time-dependent external perturbation, and to derive the associated polarizabilities. Using time-dependent perturbation theory to obtain the expressions for the perturbed states, the first-order perturbed eigenvectors are defined as:

$$\mid n(t) >= e^{\frac{-\imath E_n^{(0)} t}{\hbar}} \mid n^{(0)} > \ + \ \sum_{s \neq n} c_s(t) e^{\frac{-\imath E_s^{(0)} t}{\hbar}} \mid s^{(0)} > \tag{3.16}$$

where $c_s(t)$ are the first-order mixing coefficients given by perturbation theory in the form:

$$c_s(t) = \frac{-\imath}{\hbar} \int_0^t dt \ e^{\imath \omega_{sn} t} < s^{(0)} \mid H_1 \mid n^{(0)} > \tag{3.17}$$

$\mid n^{(0)} >$ and $\mid s^{(0)} >$ are eigenvalues of the unperturbed Hamiltonian and $\omega_{ns} = \frac{E_n - E_s}{\hbar}$. Substituting in this formula the Hamiltonian H_1, previously defined in equation (3.9), it is possible to derive the expression for the coefficients $c_s(t)$ in terms of the fields and their derivatives, up to the electric octopole-magnetic quadrupole order:

$$\begin{aligned} c_s(t) \ &= \ \frac{e^{-\imath\omega_{ns} t}}{\hbar(\omega^2 - \omega_{ns}^2)} \{ < p_i >_{sn} [\omega_{ns} E_i(t) - \imath \dot{E}_i(t)] \\ &\quad + \frac{1}{2} < q_{\imath\jmath} >_{sn} [\omega_{ns} E_{\imath\jmath}(t) - \imath \dot{E}_{\imath\jmath}(t)] \\ &\quad + \frac{1}{6} < q_{\imath\jmath k} >_{sn} [\omega_{ns} E_{\imath\jmath k}(t) - \imath \dot{E}_{\imath\jmath k}(t)] + \ldots \\ &\quad + \ < m_{\imath} >_{sn} [\omega_{ns} B_i(t) - \imath \dot{B}_i(t)] \\ &\quad + \frac{1}{2} < m_{\imath\jmath} >_{sn} [\omega_{ns} B_{\imath\jmath}(t) - \imath \dot{B}_{\imath\jmath}(t)] + \ldots \} \end{aligned} \tag{3.18}$$

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[6] I will discuss in detail the magnetizability operator later in this section.

Note that the form of eq. (3.18) has been obtained using time-dependent perturbation theory[28] and integrating by part in eq. (3.17), so that time derivatives of the fields, $\dot{E}$ and $\dot{B}$, appear in it. To evaluate the previous coefficients, without loss of generality, I have considered an external electromagnetic perturbation represented by harmonic plane waves of the form:

$$\boldsymbol{E} = \boldsymbol{E}_0 \cos(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t) \qquad \boldsymbol{B} = \boldsymbol{B}_0 \cos(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t) \tag{3.19}$$

Here $\boldsymbol{k}$ is the wave vector and ω the frequency of the external fields. The expectation value of a multipole moment operator Ω can be defined as:

$$\begin{aligned} < n(t) \mid \Omega \mid n(t) > \; &= \; < \Omega^{(0)} >_{nn} + < \Omega^{(1)} >_{nn} \\ &\quad + 2 \sum_{s \neq n} Re\{c_s e^{i\omega_{ns} t} < \Omega^{(0)} >_{ns}\} \end{aligned} \tag{3.20}$$

where the unperturbed part $\Omega^{(0)}$ and the perturbed part $\Omega^{(1)}$ of the operator have been separated. The latter contribution is derived from the action of the external magnetic field for a magnetic moment. Thus, the total electric and magnetic multipole moments up to the electric octopole-magnetic quadrupole order are defined as:

$$\begin{aligned} < n(t) \mid p_i \mid n(t) > \; &= \; p_i^{(0)} + \alpha_{ij} E_j(t) + \frac{1}{\omega} \alpha'_{ij} \dot{E}_j(t) \\ &\quad + \frac{1}{2} a_{ijk} E_{jk}(t) + \frac{1}{2\omega} a'_{ijk} \dot{E}_{ij}(t) \\ &\quad + \frac{1}{6} b_{ijkl} E_{jkl}(t) + \frac{1}{6\omega} b'_{ijkl} \dot{E}_{jkl}(t) + \dots \\ &\quad + G_{ij} B_j(t) + \frac{1}{\omega} G'_{ij} \dot{B}_j(t) \\ &\quad + \frac{1}{2} H'_{ijk} B_{jk}(t) + \frac{1}{2\omega} H'_{ijk} \dot{B}_{jk}(t) + \dots \end{aligned} \tag{3.21}$$

$$\begin{aligned} < n(t) \mid q_{ij} \mid n(t) > \; &= \; q_{ij}^{(0)} + \mathsf{a}_{ijk} E_k(t) + \frac{1}{\omega} \mathsf{a}'_{ijk} \dot{E}_k(t) \\ &\quad + \frac{1}{2} d_{ijkl} E_{kl}(t) + \frac{1}{2\omega} d'_{ijkl} \dot{E}_{kl}(t) + \dots \\ &\quad + L_{ijk} B_k(t) + \frac{1}{\omega} L'_{ijk} \dot{B}_k(t) + \dots \end{aligned} \tag{3.22}$$

$$< n(t) \mid q_{ijk} \mid n(t) >= q_{ijk}^{(0)} \; + \; \mathsf{b}_{ijkl} E_l(t) \; + \; \frac{1}{\omega} \; \mathsf{b}'_{ijkl} \dot{E}_k(t) \; + \; \dots \tag{3.23}$$

$$\begin{aligned} (3.24)\quad < n(t) \mid m_\imath \mid n(t) > \; &= \; m_i^{(0)} + \mathcal{G}_{\imath\jmath} E_\jmath(t) + \frac{1}{\omega}\mathcal{G}'_{\imath\jmath}\dot{E}_\jmath(t) \\ &\quad + \frac{1}{2}\mathcal{L}_{\imath\jmath k} E_{\jmath k}(t) + \frac{1}{2\omega}\mathcal{L}'_{\imath\jmath k}\dot{E}_{\jmath k}(t) + \ldots \\ &\quad + \chi_{\imath\jmath} B_\jmath(t) + \frac{1}{\omega}\chi'_{\imath\jmath}\dot{B}_\jmath(t) + \ldots \end{aligned}$$

$$(3.25)\qquad < n(t) \mid m_{\imath\jmath} \mid n(t) >= m_{\imath\jmath}^{(0)} \; + \; \mathcal{H}_{\imath\jmath k} E_k(t) \; + \; \frac{1}{\omega}\; \mathcal{H}'_{\imath\jmath k}\dot{E}_k(t) \; + \; \ldots$$

In these formulas several multipole polarizabilities have been defined. For a charge distribution originating in an external time-dependent electromagnetic field, their expressions are[1]:

$$(3.26)\qquad \alpha_{\imath\jmath} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} Re\{< p_\imath >_{ns} < p_\jmath >_{sn}\} \; = \; \alpha_{\jmath\imath}$$

$$(3.27)\qquad \alpha'_{\imath\jmath} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} Im\{< p_\imath >_{ns} < p_\jmath >_{sn}\} \; = \; -\alpha'_{\jmath\imath}$$

$$(3.28)\qquad a_{\imath\jmath k} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} Re\{< p_\imath >_{ns} < q_{\jmath k} >_{sn}\} \; = \; \mathsf{a}_{\jmath k\imath}$$

$$(3.29)\qquad a'_{\imath\jmath k} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} Im\{< p_\imath >_{ns} < q_{\jmath k} >_{sn}\} \; = \; -\mathsf{a}'_{\jmath k\imath}$$

$$(3.30)\qquad G_{\imath\jmath} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} Re\{< p_\imath >_{ns} < m_\jmath >_{sn}\} \; = \; \mathcal{G}_{\jmath\imath}$$

$$(3.31)\qquad G'_{\imath\jmath} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} Im\{< p_\imath >_{ns} < m_\jmath >_{sn}\} \; = \; -\mathcal{G}_{\jmath\imath}$$

$$(3.32)\qquad b_{\imath\jmath kl} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} Re\{< p_\imath >_{ns} < q_{\jmath kl} >_{sn}\} \; = \; \mathsf{b}_{\jmath kl\imath}$$

$$(3.33)\qquad b'_{\imath\jmath kl} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} Im\{< p_\imath >_{ns} < q_{\jmath kl} >_{sn}\} \; = \; -\mathsf{b}'_{\jmath kl\imath}$$

$$d_{\imath\jmath kl} = \frac{2}{\hbar}\sum_{s} \omega_{sn} Z_{sn} Re\{< q_{\imath\jmath} >_{ns} < q_{kl} >_{sn}\} \;=\; d_{kl\imath\jmath} \tag{3.34}$$

$$d'_{\imath\jmath kl} = -\frac{2}{\hbar}\sum_{s} \omega Z_{sn} Im\{< q_{\imath\jmath} >_{ns} < q_{kl} >_{sn}\} \;=\; -d'_{kl\imath\jmath} \tag{3.35}$$

$$H_{\imath\jmath k} = \frac{2}{\hbar}\sum_{s} \omega_{sn} Z_{sn} Re\{< p_{\imath} >_{ns} < m_{\jmath k} > sn\} \;=\; \mathcal{H}_{\jmath k\imath} \tag{3.36}$$

$$H'_{\imath\jmath k} = -\frac{2}{\hbar}\sum_{s} \omega Z_{sn} Im\{< p_{\imath} >_{ns} < m_{\jmath k} >_{sn}\} \;=\; -\mathcal{H}'_{\jmath k\imath} \tag{3.37}$$

$$L_{\imath\jmath k} = \frac{2}{\hbar}\sum_{s} \omega_{sn} Z_{sn} Re\{< q_{\imath\jmath} >_{ns} < m_{k} >_{sn}\} \;=\; L_{\jmath\imath k} \;=\; \mathcal{L}_{k\imath\jmath} \tag{3.38}$$

$$L'_{\imath\jmath k} = -\frac{2}{\hbar}\sum_{s} \omega Z_{sn} Im\{< q_{\imath\jmath} >_{ns} < m_{k} >_{sn}\} \;=\; L'_{\jmath\imath k} \;=\; -\mathcal{L}'_{k\imath\jmath} \tag{3.39}$$

$$\begin{aligned} \chi_{\imath\jmath} \;=\;& \frac{2}{\hbar}\sum_{s} \omega_{sn} Z_{sn} Re\{< m_{\imath} >_{ns} < m_{\jmath} >_{sn}\} \\ &+ \sum_{\alpha=1}^{N} \frac{(q^{(\alpha)})^2}{4m^{(\alpha)}} \langle r_{\imath}^{(\alpha)} r_{\jmath}^{(\alpha)} - (r^{(\alpha)})^2 \delta_{\imath\jmath} \rangle_{nn} = \chi_{\jmath\imath} \end{aligned} \tag{3.40}$$

$$\chi'_{\imath\jmath k} = -\frac{2}{\hbar}\sum_{s} \omega Z_{sn} Im\{< m_{\imath} >_{ns} < m_{\jmath} > sn\} \;=\; -\chi'_{\jmath\imath} \tag{3.41}$$

where

$$Z_{sn} \;=\; (\omega_{sn}^2 \;-\; \omega^2)^{-1} \tag{3.42}$$

Considering the polarizability expressions just obtained, let us analyze their properties taking in account the Hermiticity of the multipole moment operators. At first it is possible to recognize how the static results could be recovered taking the limit for $\omega \to 0$; in particular, the imaginary terms vanish, confirming the fact that they describe the induction of a multipole moment given by the time derivatives of the fields. Furthermore, it is useful to classify the polarizabilities with respect to their multipole order and to their symmetries. Referring to the latter property, two kind of symmetries can be recognized: intrinsic symmetries, manifestly gathered from their explicit expressions, and symmetries depending on the geometric and time-reversal nature of the properties. The former kind of symmetries, such as $a_{\imath\jmath k} = a_{\imath k\jmath}$ or $b_{\imath\jmath kl} = b_{\imath\jmath lk} = b_{\imath k\jmath l}$ etc. are directly obtained using symmetry permutations of the multipole operators and the quantum mechanical expressions, whereas the second kind of symmetries have to be treated in more detail. Considering group theory, and doing some geometrical observations about the behavior of a tensor under inversion of axis and rotations, a generic tensor can be classified as polar, axial or isotropic. By definition, a second-rank Cartesian tensor $T_{\imath\jmath}$ satisfy the relations[31]:

$$T'_{\imath\jmath} = l_{\imath r} l_{\jmath s} T_{rs} \tag{3.43}$$

$$T'_{\imath\jmath} = \pm l_{\imath r} l_{\jmath s} T_{rs} \tag{3.44}$$

for polar and axial tensors respectively, where the plus and minus sign applies for a proper or improper transformation, respectively. Here $l_{\imath r}$ is named the direction cosine, and it specifies the relative orientation of two sets of Cartesian axis. It follows that a vector is simply a one-rank tensor, polar or axial according to whether it changes sign or not with respect to the inversion of the axis. A tensor is moreover called isotropic, if each of its components retain the same values under an arbitrary rotation of the axis.

Time symmetry is obtained by defining a time reversed-operator T as $T = UK$, where K is the complex conjugation operator and U is a unitary operator, and applying it to a general operator Ω, so that $\Omega' = T\Omega T^{-1}$. Thus a tensor is said to be time-even if $\Omega' = \Omega$, or time-odd if $\Omega' = -\Omega$.

Spatial-time symmetries are a wide topic that has been treated in details elsewhere Ref.([26],[27],[28]), so it would be possible to extend this analysis and go through several details. However, for my purpose it is sufficient to consider the results achieved by this theory and use them in order to classify the polarizability tensors, and simplify calculations and expressions.

Going back to the polarizability expressions, the quantity $Z_{sn} = (\omega_{sn}^2 - \omega^2)^{-1}$ appeared in these equations. It is trivial to note that this quantity goes to infinity at resonance, namely when the frequency of the external field ω equals the frequency ω_{sn}, corresponding to the transition energies between the electronic levels s and n. Obviously, this is an unphysical result, so it is necessary redefine the expression for Z_{sn} as $Z_{sn} = f + \imath g$, where f and g are the dispersion and absorption line shape functions. In this way Z_{sn} is a complex function, with poles corresponding to the transition energies and with dependencies from ω, ω_{sn} and Γ_{sn}, where Γ_{sn} is the damping factor and it is related to the electronic transition sn and to the width of the absorption (or resonance) curve[31],[1]. In this thesis the discussion is restricted to the case where the frequency of the external field ω assumes values far from the transition frequency ω_{sn}, e.g.optical frequencies, so that the expression $Z_{sn} = (\omega_{sn}^2 - \omega^2)^{-1}$ will never be zero. In a completely general case, a more precise definition has to be used.

3.3 The origin-dependence of molecular properties

Multipole moments are origin dependent, since they are defined with respect to an expansion point. Operating a shift of the origin of the coordinates in the definitions of multipole moments, it is possible to see how their expressions give rise to an additional term due to the displacement of the reference system. The most trivial example is the electric dipole moment $p_\imath$. Giving a shifting vector $\boldsymbol{d}$, let consider the displacement of the position operator:

$$\boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{d} \tag{3.45}$$

that when substituted into the definition of the electric dipole moment

$$p_\imath = \sum_\alpha q^{(\alpha)} r_\imath^{(\alpha)}$$

leads to:

$$p'_\imath = p_\imath - d_\imath \sum_\alpha q^{(\alpha)} = p_\imath + \Delta p_\imath \tag{3.46}$$

where $\Delta p_\imath$ is the displacement term. Following the same procedure, it is possible to obtain the displacement terms that appear for all the electric and magnetic moment operators. Since molecular properties are obtained as expectation value of the moment operators, the polarizability tensors have to be origin dependent as well. Knowing how to calculate the displacement terms, it is easy to redefine all the expressions of the polarizabilities, showing that an additional term given by the shift of the origin appears:

$$< \Omega' >_{nn} = < \Omega >_{nn} + < \Delta\Omega >_{nn} \tag{3.47}$$

Explicit expressions of the displacement terms $< \Delta\Omega >_{nn}$ for the different polarizability tensors are:

$$\Delta\alpha_{\imath\jmath} = 0 \tag{3.48}$$

$$\Delta\alpha'_{\imath\jmath} = 0 \tag{3.49}$$

$$\Delta a_{\imath\jmath k} = -d_\jmath \alpha_{\imath k} - d_k \alpha_{\imath\jmath} \tag{3.50}$$

$$\Delta a'_{\imath\jmath k} = -d_\jmath \alpha'_{\imath k} - d_k \alpha'_{\imath\jmath} \tag{3.51}$$

$$\Delta G_{\imath\jmath} = -\frac{1}{2}\omega\varepsilon_{\jmath kl} d_k \alpha'_{\imath l} \tag{3.52}$$

$$\Delta G'_{\imath\jmath} = \frac{1}{2}\omega\varepsilon_{\jmath kl} d_k \alpha_{\imath l} \tag{3.53}$$

$$\Delta b_{\imath\jmath kl} = -d_\jmath a_{\imath kl} - d_k a_{\imath\jmath l} - d_l a_{\imath\jmath k} + d_\jmath d_k \alpha_{\imath l} + d_\jmath d_l \alpha_{\imath k} + d_k d_l \alpha_{\imath\jmath} \tag{3.54}$$

$$\Delta b'_{\imath\jmath kl} = -d_\jmath a'_{\imath kl} - d_k a'_{\imath\jmath l} - d_l a'_{\imath\jmath k} + d_\jmath d_k \alpha'_{\imath l} + d_\jmath d_l \alpha'_{\imath k} + d_k d_l \alpha'_{\imath\jmath} \tag{3.55}$$

$$\begin{aligned} \Delta d_{\imath\jmath kl} \;&=\; -d_\imath a_{\jmath kl} - d_\jmath a_{\imath kl} - d_k a_{l\imath\jmath} - d_l a_{k\imath\jmath} \\ &\quad + d_\imath d_k \alpha_{\jmath l} + d_\imath d_l \alpha_{\jmath k} + d_\jmath d_k \alpha_{\imath l} + d_\jmath d_l \alpha_{\imath k} \end{aligned} \tag{3.56}$$

$$\begin{aligned} \Delta d'_{\imath\jmath kl} \;&=\; -d_\imath a'_{\jmath kl} - d_\jmath a'_{\imath kl} - d_k a l \imath \jmath' - d_l a'_{k\imath\jmath} \\ &\quad + d_\imath d_k \alpha'_{\jmath l} + d_\imath d_l \alpha'_{\jmath k} + d_\jmath d_k \alpha'_{\imath l} + d_\jmath d_l \alpha'_{\imath k} \end{aligned} \tag{3.57}$$

$$\Delta H_{\imath\jmath k} = -2d_k G_{\imath\jmath} + \frac{2}{3}\delta_{\jmath k} d_l G_{\imath l} - \frac{1}{3}\omega\varepsilon_{\jmath lm} d_l (a'_{\imath km} - 2d_k \alpha'_{\imath m}) \tag{3.58}$$

$$\Delta H_{\imath\jmath k} = -2d_k G_{\imath\jmath} + \frac{2}{3}\delta_{\jmath k} d_l G'_{\imath l} + \frac{1}{3}\omega\varepsilon_{\jmath lm} d_l (a_{\imath km} - 2d_k \alpha_{\imath m}) \tag{3.59}$$

$$\Delta L_{\imath\jmath k} = -d_\imath G_{\jmath k} - d_\jmath G_{\imath k} + \frac{1}{2}\omega\varepsilon_{klm} d_l (a'_{m\imath\jmath} + d_\imath \alpha'_{\jmath m} + d_\jmath \alpha'_{\imath m}) \tag{3.60}$$

$$\Delta L_{\imath\jmath k} = -d_\imath G'_{\jmath k} - d_\jmath G'_{\imath k} + \frac{1}{2}\omega\varepsilon_{klm} d_l (a_{m\imath\jmath} - d_\imath \alpha_{\jmath m} - d_\jmath \alpha_{\imath m}) \tag{3.61}$$

$$\Delta\chi_{\imath\jmath} = \frac{1}{2}\omega(\varepsilon_{\imath kl} d_k G'_{l\jmath} + \varepsilon_{\jmath kl} d_k G'_{l\imath}) + \frac{1}{4}\omega^2 \varepsilon_{\imath kl}\varepsilon_{\jmath mn} d_k d_m \alpha_{ln} \tag{3.62}$$

$$\Delta\chi'_{\imath\jmath} = -\frac{1}{2}\omega(\varepsilon_{\imath kl} d_k G_{l\jmath} - \varepsilon_{\jmath kl} d_k G_{l\imath}) + \frac{1}{4}\omega^2 \varepsilon_{\imath kl}\varepsilon_{\jmath mn} d_k d_m \alpha'_{ln} \tag{3.63}$$

3.4 Remarks

Let me briefly recapitulate what I have discussed so far.

Electric and magnetic moment operators were defined and their expectation values were calculated in the framework of time-dependent perturbation theory, in the presence of an external time-dependent electromagnetic field. The expressions for the moment operators in terms of molecular properties, namely polarizabilities, have been derived and discussed.

Observing the formulas above, eqs. (3.48)-(3.63), surprising unphysical results showed up. In fact the displacement terms calculated for the molecular properties are not zero, and since molecular properties are observable quantities their expressions should not be origin dependent. More precisely, the polarizabilities themselves are not origin dependent, but some of the expressions derived above have an explicit dependence on the origin. In particular, we can see how the polarizabilities corresponding to the electric dipole-electric dipole order are origin independent, eqs. (3.48) and (3.49), whereas the rest of the displacement terms Δ are not zero. These displacements are expressed in terms of other polarizabilities (α_{ij},G_{ij} etc.), which are themselves frequency-dependent.

Noting that we are treating observable quantities, it becomes necessary to redefine the expressions for molecular properties as linear combination of the polarizabilities of the same higher multipole order, in order to derive origin-independent definitions for them. This means consider contributions that appear at the same order in the multipole expansions of the vector and of the scalar potentials given in eqs. (3.3) and (3.4). Following this procedure, the intrinsic symmetry degree of freedom is lowered, reducing the number of the polarizabilities included in each expression.

The idea to consider linear combinations of polarizabilities has been formulated by Raab and de Lange and used by the same authors to obtain an origin-independent expression of the frequency-dependent magnetizability. For this reason my discussion often make use of their procedures and notation.

3.5 The magnetizability

The treatment developed so far has been general with respect to molecular properties in a time-dependent external electromagnetic field. However, my goal is to discuss a specific second-order magnetic property, namely the magnetizability, so let us focus our attention to it. The definition of the magnetizability has been given in equation (3.40). Recalling that perturbation theory has been used and thus that we are referring to the second-order energy corrections, it is worth pointing out that this expression contains two terms, the former comes from the linear term of the vector potential in the Hamiltonian and is known as the paramagnetic part, while the latter is given by the quadratic term in the vector potential and is known as the diamagnetic part. Therefore, the expression of the magnetizability is commonly split as:

$$\chi_{\imath\jmath} = \chi^{p}_{\imath\jmath} + \chi^{d}_{\imath\jmath} \tag{3.64}$$

where

$$\chi^{p}_{\imath\jmath} = \frac{2}{\hbar}\sum_{s\neq n} \omega_{sn} Z_{sn} Re\{< m_\imath >_{ns}< m_\jmath >_{sn}\} \tag{3.65}$$

$$\chi^{d}_{\imath\jmath} = \sum_{\alpha=1}^{N} \frac{(q^{(\alpha)})^2}{4m^{(\alpha)}} \langle r^{(\alpha)}_\imath r^{(\alpha)}_\jmath - (r^{(\alpha)})^2 \delta_{\imath\jmath} \rangle_{nn} \tag{3.66}$$

Here $< m_\imath >$ is the transition moment of the magnetic dipole operator, defined in the non-relativistic framework when the spin contribution is neglected, namely: $m_\imath = -\frac{1}{2} l_\imath = -\frac{1}{2}(\boldsymbol{r} \wedge \boldsymbol{p})_\imath = \frac{\imath}{2}(\boldsymbol{r} \wedge \nabla)_\imath$, where $\boldsymbol{p}$ is the linear momentum operator, which in the position representation is defined as $\boldsymbol{p} = -\imath\hbar\nabla$; while $\boldsymbol{r}$ is the position operator and $\delta_{\imath\jmath}$ is the Dirac's delta. Note that the summation in the diamagnetic term is extended to all the electrons in the system, while the sum in the paramagnetic term is over all the possible energy states s. It is useful to rewrite the paramagnetic and the diamagnetic parts in terms of the angular momentum operator $\boldsymbol{l} = -\imath\hbar\boldsymbol{r} \wedge \nabla$ and using response theory[14], to express the magnetizability in the form[7]:

$$\boldsymbol{\chi}^{p} = -\frac{e^2}{4m^2} \ll \boldsymbol{l}; \boldsymbol{l} \gg_\omega \tag{3.67}$$

$$\boldsymbol{\chi}^{d} = -\frac{e^2}{4m^2} \ll \boldsymbol{r} \wedge \boldsymbol{l}; \boldsymbol{p} \gg_\omega \tag{3.68}$$

Then, by definition, the magnetizability appears as a time-even, second-rank, symmetric, polar tensor that can be split in two terms representing the diamagnetic and the paramagnetic parts. Inserting a displacement of the origin

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[7] This form of the paramagnetic and diamagnetic contributions will be used later in this chapter.

of the coordinates in its expressions, and recalling the displacement terms given in eqs. (3.62) and (3.63), it is also possible to state that, in the general case, the magnetizability is an origin-dependent quantity, since $\Delta\chi_{ij}$ and $\Delta\chi'_{ij}$ are not zero. In order to discuss in detail this fact, let distinguish the case for a time-independent and for a time-dependent external perturbation. In fact, we will observe that in the former case the magnetizability turns out to be an origin-independent quantity, whereas in the latter case it is not possible avoid the origin dependence of its expression.
Let us now consider the frequency-independent magnetizability.

3.5.1 Frequency-independent magnetizability

For a time-independent external magnetic field, the magnetizability is origin-independent for a complete, variational basis set. This result was first achieved by J.H.Van Vleck[5], and subsequently recovered in several ways using the two equivalent definitions of the magnetizability given above. In the following discussion, I will show one possible method to reach this conclusion, where the paramagnetic and the diamagnetic parts will be treated independently; it will become clear that the origin dependence will be exactly the same for both terms, but with opposite signs, so that the two Δ-contributions will cancel each other. Another possible way to recover this result is described in the Appendix A.
Let us consider the expression for the energy correction given by perturbation theory to second-order. By virtue of the previous analysis, two terms contribute to the second-order magnetic property, namely:

$$E^{d}_{(2)} = \frac{e^2}{2m} < 0 \mid \boldsymbol{A} \cdot \boldsymbol{A} \mid 0 >_{\omega=0} \tag{3.69}$$

$$E^{p}_{(2)} = \frac{e^2}{2m} \ll \boldsymbol{A} \cdot \boldsymbol{p}; \boldsymbol{A} \cdot \boldsymbol{p} \gg_{\omega=0} \tag{3.70}$$

In this approach, a shift of the origin of the coordinates can be interpreted as a change of gauge. So far, no gauge choice has been made yet, so we can freely choose a vector potential of the form:

$$\boldsymbol{A} = \frac{1}{2}\boldsymbol{B} \wedge (\boldsymbol{r} - \boldsymbol{r}_o) \tag{3.71}$$

Taking $\boldsymbol{r}' = \boldsymbol{r}_o + \boldsymbol{d}$[8], the vector potential becomes[29]:

$$\boldsymbol{A}' = \boldsymbol{A} + \nabla\Lambda = \frac{1}{2}\boldsymbol{B} \wedge (\boldsymbol{r} - \boldsymbol{r}') \tag{3.72}$$

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[8] Where $\boldsymbol{r}_o$ is the gauge origin and $\boldsymbol{d}$ the shift.

where I have been introduced the gauge function:

$$\Lambda = -\frac{1}{2}(\boldsymbol{B} \wedge \boldsymbol{d}) \cdot (\boldsymbol{r} - \boldsymbol{r}_o) \tag{3.73}$$

Based on the gauge freedom, it is equivalent to choose a function Λ of this form, instead of a shift of the origin, and recover the same results. Note that this specific choice of the vector potential satisfy the Coulomb gauge, but this is just a matter of facts and it is not relevant in my discussion, since the same procedure can be applied with different gauges.

Let us now substitute the shifted vector potential $\boldsymbol{A'}$ in the second-order energy correction defined by eqs. (3.69) and (3.70), and separately examine the paramagnetic and the diamagnetic terms. The energy is expressed as a function of the external static magnetic field and of the position operators $\boldsymbol{r}$ and $\boldsymbol{r}_0$. Doing algebraic manipulations and keeping in mind that the second-order energy can be written in the form:

$$E_{(2)} = \frac{1}{2}\boldsymbol{B}^T \cdot \boldsymbol{\chi} \cdot \boldsymbol{B} = \frac{1}{2}\boldsymbol{B}^T \cdot (\boldsymbol{\chi}^p + \boldsymbol{\chi}^d) \cdot \boldsymbol{B} \tag{3.74}$$

the diamagnetic term becomes:

$$\begin{aligned} \boldsymbol{\chi}^{d\prime} \;=\; \boldsymbol{\chi}^d \;+\; & \frac{e^2}{4m}\{< 0 \mid (\boldsymbol{r} - \boldsymbol{r}_o \cdot \boldsymbol{d} - \boldsymbol{d}(\boldsymbol{r} - \boldsymbol{r}_o)^T \mid 0 > \\ & + < 0 \mid \boldsymbol{d} \cdot (\boldsymbol{r} - \boldsymbol{r}_o) - (\boldsymbol{r} - \boldsymbol{r}_o)\boldsymbol{d}^T \mid 0 > \\ & - < 0 \mid \boldsymbol{d} \cdot \boldsymbol{d} - \boldsymbol{d}\boldsymbol{d}^T \mid 0 >\} \end{aligned} \tag{3.75}$$

At this point, it is necessary to make use of the hypervirial relation, valid for an exact theory and in certain approximations such as the RPA (Random Phase Approximation), when using a complete variational orbital basis set [14]:

$$\frac{\imath\hbar}{m}\boldsymbol{p} = [\boldsymbol{r}, H] \tag{3.76}$$

and of the following equalities:

$$\begin{aligned} [\boldsymbol{d} \wedge \boldsymbol{l}, \boldsymbol{r}] &= \imath\hbar(\boldsymbol{r} \cdot \boldsymbol{d} - \boldsymbol{r}\boldsymbol{d}^T), \\ < 0 \mid \boldsymbol{r} \cdot \boldsymbol{r} - \boldsymbol{r}\boldsymbol{r}^T \mid 0 > &= \frac{1}{\imath\hbar} \ll \boldsymbol{r} \wedge \boldsymbol{l}; [\boldsymbol{r}, H] \gg_{\omega=0}, \\ < 0 \mid [A, B] \mid 0 > &= \ll A; [B, H] \gg_{\omega=0} \end{aligned} \tag{3.77}$$

Thus, the diamagnetic term can be reformulated as:

$$\begin{aligned} \boldsymbol{\chi}^{d\prime} \;=\; \boldsymbol{\chi}^d \;+\; & \frac{e^2}{4m^2}\{\ll \boldsymbol{d} \wedge \boldsymbol{l}(\boldsymbol{r} - \boldsymbol{r}_o); \boldsymbol{p} \gg_{\omega=0} \\ & + \ll (\boldsymbol{r} - \boldsymbol{r}_o) \wedge \boldsymbol{l}(\boldsymbol{d}); \boldsymbol{p} \gg_{\omega=0} - \ll \boldsymbol{d} \wedge \boldsymbol{l}(\boldsymbol{d}); \boldsymbol{p} \gg_{\omega=0}\} \end{aligned} \tag{3.78}$$

In the same way, using the vector potential $\boldsymbol{A}'$ and by comparison with the second-order energy, the paramagnetic term can be rewritten as:

$$\begin{aligned}\boldsymbol{\chi}^{p\prime} &= \boldsymbol{\chi}^{p} + \frac{e^2}{4m^2}\{\ll \boldsymbol{l}(\boldsymbol{r}-\boldsymbol{r}_o);\boldsymbol{l}(\boldsymbol{d}) \gg_{\omega=0} \\ &\quad + \ll \boldsymbol{l}(\boldsymbol{d});\boldsymbol{l}(\boldsymbol{r}-\boldsymbol{r}_o) \gg_{\omega=0} - \ll \boldsymbol{l}(\boldsymbol{d});\boldsymbol{l}(\boldsymbol{d}) \gg_{\omega=0}\}\end{aligned} \tag{3.79}$$

Note that:

$$\ll \boldsymbol{l}(\boldsymbol{d});\boldsymbol{l}(\boldsymbol{r}-\boldsymbol{r}_o) \gg_{\omega=0} = \ll \boldsymbol{l}(\boldsymbol{r}-\boldsymbol{r}_o);\boldsymbol{l}(\boldsymbol{d}) \gg_{\omega=0}$$

so, by exploiting the relations introduced above and by some algebraic manipulations, the paramagnetic term becomes:

$$\begin{aligned}\boldsymbol{\chi}^{p\prime} &= \boldsymbol{\chi}^{p} - \frac{e^2}{4m^2c^2}\{\ll \boldsymbol{d}\wedge\boldsymbol{l}(\boldsymbol{r}-\boldsymbol{r}_o);\boldsymbol{p} \gg_{\omega=0} \\ &\quad + \ll (\boldsymbol{r}-\boldsymbol{r}_o)\wedge\boldsymbol{l}(\boldsymbol{d});\boldsymbol{p} \gg_{\omega=0} - \ll \boldsymbol{d}\wedge\boldsymbol{l}(\boldsymbol{d});\boldsymbol{p} \gg_{\omega=0}\}\end{aligned} \tag{3.80}$$

As stated before and confirmed by the above calculations, the additional terms given by the origin displacements vanish so that, in the presence of a time-independent external perturbation, the magnetizability is origin independent, for a complete, variational basis set or, alternatively, for methods satisfying eq. (3.76).

$$\boldsymbol{\chi}^{p\prime} + \boldsymbol{\chi}^{d\prime} = \boldsymbol{\chi}^{p} + \boldsymbol{\chi}^{d} \tag{3.81}$$

The demonstration performed here highlights the roles played by the gauge choice in the analysis of the origin dependence of molecular properties. In particular, it is possible to look at the shift of the origin as a specific choice of gauge, and therefore consider a special class of gauge transformations, e.g. Λ defined above. To this end, it is worth to note that the multipole gauge leads to cumbersome calculations, but at the same time to useful, general expressions of molecular properties, in the presence of external perturbations. In fact, looking at the definition of the magnetizability given in equation (3.40) and to the origin displacement given in equation (3.62), both obtained using the multipole gauge by Raab and de Lange, it is trivial to conclude that for a time-independent perturbation, i.e. setting $\omega = 0$, the origin-independence is immediately recovered without any further calculations.
Before going on, I would like to point out an assumption that has been used in the above discussion, but not explicitly expressed yet: I have only considered isotropic samples, so that no dispersion phenomena appear in the

system. Anyway, this does not lead to any loss of generality, and the dispersion relations can be included in the discussion[9].

3.5.2 Frequency-dependent magnetizability

Let now turn the attention to the frequency-dependent magnetizability. As we have seen, eqs. (3.62) and (3.63) and in the previous section, in the presence of a time-dependent magnetic field, the magnetizability is no longer origin independent, not even working with a complete basis set, so the definition given for this observable has to be modified in order to obtain an origin-independent expression. It has already been hinted that a suitable approach to derive origin-independent expressions for molecular properties is to consider linear combinations of polarizabilities beyond the electric-dipole approximation, considering terms of the same higher multipole order in the multipole expansion of the potentials. This is exactly the idea used by Raab and de Lange[6] to pursue an origin-independent expression of the frequency-dependent magnetizability. Let analyze their procedure within the framework introduced above, and using the definitions of the polarizabilities given in the equations (3.26)-(3.41).

The definition of χ says that the magnetizability is a time even, second-rank, symmetric, polar tensor, therefore it is necessary to look for an expression that fulfill these requirements. The hypothesis to restrict the analysis to non-magnetic molecules has been done without loss of generality, there are thus five polarizability tensors that contribute to the expression of the magnetizability up to the electric octopole-magnetic dipole order. Reducing the discussion to only time-even tensors, the expectation values of the five moment operators are:

$$< p_\imath >_{nn} = \frac{1}{6} b_{\imath\jmath kl} E_{\jmath kl}(t) + \frac{1}{2\omega} H'_{\imath\jmath k} \dot{B}_{\jmath k}(t) \tag{3.82}$$

$$< q_{\imath\jmath} >_{nn} = \frac{1}{2} d_{\imath\jmath kl} E_{kl}(t) + \frac{1}{\omega} L'_{\imath\jmath k} \dot{B}_k(t) \tag{3.83}$$

$$< q_{\imath\jmath k} >_{nn} = b_{l\imath\jmath k} E_l \tag{3.84}$$

$$< m_\imath >_{nn} = \frac{1}{2\omega} L'_{\imath\jmath k} \dot{E}_{\jmath k}(t) + \chi_{\imath\jmath} B_\jmath(t) \tag{3.85}$$

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[9] Non-isotropic samples show dispersion phenomena, so it is necessary consider off-diagonal elements of the tensors that describe molecular properties; viceversa for isotropic samples it is possible to consider only their trace.

$$< m_{\imath\jmath} >_{nn} = -\frac{1}{\omega} H'_{\imath\jmath k} \dot{E}_k(t) \tag{3.86}$$

where the definitions given in eqs. (3.26)-(3.41) have been used. The idea to simplify the expressions of the quoted five tensors has been formulated by Raab and de Lange[6], exploiting the hypothesis to consider a non-magnetic molecule, and reducing to real wave functions[30]. Let us investigate the properties of the tensors included in the analysis. Looking at the expectation values of the moment operators, we can see that $b_{\imath\jmath kl}$, $d_{\imath\jmath kl}$ and $\chi_{\imath\jmath}$ are polar tensors, whereas $H'_{\imath\jmath k}$ and $L'_{\imath\jmath k}$ are axial tensors. Using the permutation symmetry of $q_{\imath\jmath}$ and $q_{\imath\jmath k}$ and the Hermiticity of $q_{\imath\jmath k}$ and $m_\imath$, it is also possible to deduce the intrinsic symmetries:

$$b_{\imath\jmath kl} = b_{\imath\jmath lk} = b_{\imath k\jmath l} \quad , \quad d_{\imath\jmath kl} = d_{\jmath\imath kl} = d_{kl\imath\jmath} \quad , \quad L'_{\imath\jmath k} = L'_{\jmath\imath k} \quad , \quad \chi_{\imath\jmath} = \chi_{\imath\jmath} \tag{3.87}$$

At this point, most of the information needed to construct an origin-independent expression for $\chi_{\imath\jmath}$ are known. Therefore, it is possible to state and remark the conditions that this expression has to satisfy, also referring to the static case.

a The magnetizability has to be origin independent, so that $\Delta\chi_{\imath\jmath}(\omega) = 0$.

b The magnetizability is a time-even, second-rank, symmetric, polar tensor $\chi_{\imath\jmath} = \chi_{\jmath\imath}$.

c The external fields are weak enough, so that it is possible to work within the perturbation theory approximation, and the magnetizability will be linear in terms of the polarizabilities considered.

d Taking the limit for $\omega = 0$, the expression obtained in the static case has to be recovered.

Considering the four polarizability tensors $b_{\imath\jmath kl}$, $d_{\imath\jmath kl}$, $H'_{\imath\jmath k}$, $L'_{\imath\jmath k}$ present in the moment operators selected above, and using the Levi-Civita tensor and the Dirac's delta tensor, it has been tried to obtain a time-even, second-rank, polar symmetric tensor. By virtue of the previous observations, nine tensors have to be considered[6], namely:

1. $\varepsilon_{\imath kl} H'_{\jmath kl} + \varepsilon_{\jmath kl} H'_{\imath kl}$
2. $\varepsilon_{\imath kl} H'_{k\jmath l} + \varepsilon_{\jmath kl} H'_{k\imath l}$
3. $\varepsilon_{\imath kl} L'_{\jmath kl} + \varepsilon_{\jmath kl} L'_{\imath kl}$
4. $b_{\imath\jmath kk} + b_{\jmath\imath kk}$

5. $b_{kk\imath\jmath}$
6. $d_{\imath k\jmath k}$
7. $\delta_{\imath\jmath}\varepsilon_{klm}H'_{klm}$
8. $\delta_{\imath\jmath}b_{kkll}$
9. $\delta_{\imath\jmath}d_{klkl}$

Let us discuss in more detail the arguments that have reduced the analysis to a restricted set of nine tensors, ignoring some others.

a' $H'_{\jmath kl}$ and $L'_{\imath kl}$ are axial tensors, so that given that the magnetizability has to be a polar tensor, these tensors have to appear linearly combined with the Levi-Civita tensor, satisfying the definitions given in eqs. (3.43) and (3.44).

b' The linear combination $\varepsilon_{\imath kl}H'_{kl\jmath} + \varepsilon_{\jmath kl}H'_{kl\imath}$ has not been included in the previous list, because it is equivalent to the combination of tensors 1, 2 and 7. As a matter of fact, using the tensor identity $T_{\imath\jmath} = T_{\jmath\imath} + \varepsilon_{\imath\jmath k}\varepsilon_{lmk}T_{lm}$, this symmetric tensor becomes equal to $-(\varepsilon_{\imath kl}H'_{\jmath kl} + \varepsilon_{\jmath kl}H'_{\imath kl}) + \varepsilon_{\imath kl}H'_{k\jmath l} + \varepsilon_{\jmath kl}H'_{k\imath l} + \delta_{\imath\jmath}\varepsilon_{klm}H'_{klm}$.

c' The polarizability $d_{\imath\jmath kl}$ appears only in the expression for the electric quadrupole moment, and it is coupled to the term $E_{kl}(t)$. The symmetric tensors $d_{\imath\jmath kk}$ and $\delta_{\imath\jmath}d_{kkll}$ do not have to be considered, because their trace couples to $E_{\imath\jmath}(t)(\imath = \jmath)$, which is zero for transverse waves.

Coming back to the original idea of deriving an origin-independent expression of the magnetizability considering linear combinations of polarizabilities of the same higher multipole order, and taking into account all the previous statements, it is natural to write[7]:

$$\begin{aligned} \chi_{\imath\jmath}(\omega) = \chi_{\imath\jmath}(0) &+ a_1(\varepsilon_{\imath kl}H'_{\jmath kl} + \varepsilon_{\jmath kl}H'_{\imath kl}) \\ &+ a_2(\varepsilon_{\imath kl}H'_{k\jmath l} + \varepsilon_{\jmath kl}H'_{k\imath l}) + a_3(\varepsilon_{\imath kl}L'_{\jmath kl} + \varepsilon_{\jmath kl}L'_{\imath kl}) \\ &+ a_4(b_{\imath\jmath kk} + b_{\jmath\imath kk}) + a_5 b_{kk\imath\jmath} + a_6 d_{\imath k\jmath k} \\ &+ a_7\delta_{\imath\jmath}\varepsilon_{klm}H'_{klm} + a_8\delta_{\imath\jmath}b_{kkll} + a_9\delta_{\imath\jmath}d_{klkl} \end{aligned} \tag{3.88}$$

There are thus nine polarizability-independent coefficients $a_\imath$ that have to be calculated in order to get the general expression for the magnetizability. The procedure to compute these coefficients is straightforward, but quite cumbersome. At first, let us consider a displacement $\boldsymbol{d}$ of the origin of the coordinates, exactly in the same way as done before. All the origin shifts for each polarizability term have been already introduced in eqs. (3.48)-(3.63). Imposing the origin-independence given in condition a, a linear combination of nine terms that should be equal to zero is obtained, namely:

$$\begin{aligned} 0 &= \Delta\chi_{ij}(0) + a_1(\varepsilon_{ikl}\Delta H'_{jkl} + \varepsilon_{jkl}\Delta H'_{ikl}) \\ &\quad + a_2(\varepsilon_{ikl}\Delta H'_{kjl} + \varepsilon_{jkl}\Delta H'_{kil}) + a_3(\varepsilon_{ikl}\Delta L'_{jkl} + \varepsilon_{jkl}\Delta L'_{ikl}) \\ &\quad + a_4(\Delta b_{ijkk} + \Delta b_{jikk}) + a_5\Delta b_{kkij} + a_6\Delta d_{ikjk} \\ &\quad + a_7\delta_{ij}\varepsilon_{klm}\Delta H'_{klm} + a_8\delta_{ij}\Delta b_{kkll} + a_9\delta_{ij}\Delta d_{klkl} \end{aligned} \tag{3.89}$$

Now it is necessary to insert the explicit expressions for all the displacements. In this way, using the symmetry properties listed above, it is possible to collect terms in such a manner that we get a linear combination of nine independent quantities, where each of their coefficients is a function of a_i. From the definition of linear independence, nine equations for the a_i coefficients are derived, and each coefficient can be computed. The calculus give the following results:

$$\begin{gathered} a_1 = a_3 = -a_7 = -\frac{1}{2}\omega \quad , \quad a_2 = a_5 = 0, \\ a_4 = -a_8 = \frac{1}{6}\omega^2 \quad , \quad a_6 = -\frac{1}{4}\omega^2 \quad , \quad a_9 = \frac{1}{8}\omega^2 \end{gathered} \tag{3.90}$$

Therefore, the origin-independent expression for the frequency-dependent magnetizability is:

$$\begin{aligned} \chi_{ij}(\omega) &= \chi_{ij}(0) - \frac{1}{2}\omega\{\varepsilon_{ikl}(H'_{jkl} + L'_{jkl}) \\ &\quad + \varepsilon_{jkl}(H'_{ikl} + L'_{ikl}) - \omega[\frac{1}{3}(b_{ijkk} + b_{jikk}) - \frac{1}{2}d_{ikjk}] \\ &\quad - \delta_{ij}[\varepsilon_{klm}H'_{klm} - \omega(\frac{1}{3}b_{kkll} - \frac{1}{4}d_{klkl})]\} \end{aligned} \tag{3.91}$$

Observing the final result, it is clear that this expression satisfies the requirements (a)-(d), and in particular that the static limit is immediately recovered when ω is set to 0. Furthermore, it is possible to note that modifying the starting set of tensors, (1.)-(9.), the previous construction fail, and it is no longer possible to obtain an acceptable expression that satisfy all the previous requirements; the set of tensors should therefore be carefully chosen. By virtue of the intrinsic symmetry, the magnetizability has at most six independent components, which can be further reduced considering the symmetry of the specific molecule analysed.

3.6 Discussion of Raab and de Lange expression of the magnetizability

The process used by Raab and de Lange is suitable, but it looks quite artificial, and it gives no information about the quantum-mechanical origin of their final result. In fact, no modification of the non-relativistic Hamiltonian has been done, and their origin-independent expression does not come naturally from the multipole approach, but it has been built collecting several polarizabilities, in order to get an origin-independent expression. As already mentioned in the introduction, I would not call their result with the name magnetizability, given that it does not include only the diamagnetic and the paramagnetic contributions; so I would rather consider it as a second-order magnetic property, different from the magnetizability. This is an important point to discuss, because we do not actually know what is observable or not. I would expect that the frequency-dependent magnetizability is a measurable quantity, as in the static case, but it could be that it is not, so we would be able to measure a second-order magnetic property not only described by the paramagnetic and the diamagnetic contributions. From this point of view, the idea of Raab and de Lange has to be taken into account, considering that other physical quantities, e.g. optical rotation, have been defined as a sum of several contributions given by different polarizabilities[31]. Furthermore, in chapter 5, we will see how the two quoted authors have obtained a similar expression in the macroscopic case for the inverse permeability, through a much more rigid theoretical approach.

Note that, in the Raab and de Lange derivation, the hypothesis that the magnetizability has to be symmetric is only valid assuming Kleinmann symmetry, which is not in general true for frequency-dependent properties.

In conclusion, the work of Raab and de Lange does not completely resolve the issue of origin-dependence of the magnetizability, so I would like to investigate it in more details. The idea is to look for an origin-independent expression of the frequency-dependent magnetizability in the relativistic domain, and study its non-relativistic limit.

3.7 The role of the spin

Before concluding this chapter, where an origin-independent expression of the frequency-dependent magnetizability in the limit of a complete variational basis set has been derived, I would like to briefly treat the role played by the spin in this framework. The hypothesis done at the beginning was to consider closed-shell molecules, so that the expectation value of the spin operator is zero, and therefore there are no spin contributions to the molecular properties. Now let us be more general, considering also the spin-dependent part of the Hamiltonian. To this end, it is necessary to include an additional term in the Hamiltonian, namely:

$$\sum_{\alpha} \frac{q^{(\alpha)}}{2m^{(\alpha)}} g^{(\alpha)} \boldsymbol{S}^{(\alpha)} \cdot [\nabla^{(\alpha)} \wedge \boldsymbol{A}(\boldsymbol{r}^{(\alpha)}, t)] \tag{3.92}$$

where $\boldsymbol{S}$ is the spin operator. Using the expression of the vector potential given in equation (3.3), in the multipole gauge, the general definition of the magnetic moment operators has to be modified as:

$$\begin{aligned} m_{ijk\ldots z} = & \sum_{\alpha} n \frac{q^{(\alpha)}}{4m^{(\alpha)}} [r_j^{(\alpha)} r_k^{(\alpha)} \ldots r_z^{(\alpha)} (\frac{2}{n+1} l_i^{(\alpha)} + g^{(\alpha)} S_i^{(\alpha)}) \\ & + (\frac{2}{n+1} l_i^{(\alpha)} + g^{(\alpha)} S_i^{(\alpha)}) r_j^{(\alpha)} r_k^{(\alpha)} \ldots r_z^{(\alpha)}] \end{aligned} \tag{3.93}$$

where n is the order of the multipole moments. Considering the magnetic dipole and the quadrupole moment operators, the inclusion of the spin interactions leads to the expressions:

$$m_i = \sum_{\alpha} \frac{q^{(\alpha)}}{2m^{(\alpha)}} (l_i^{(\alpha)} + g^{(\alpha)} S_i^{(\alpha)}) \tag{3.94}$$

$$m_{ij} = \sum_{\alpha} \frac{q^{(\alpha)}}{2m^{(\alpha)}} [r_j^{(\alpha)} (\frac{2}{3} l_i^{(\alpha)} + g^{(\alpha)} S_i^{(\alpha)}) + (\frac{2}{3} l_i^{(\alpha)} + g^{(\alpha)} S_i^{(\alpha)}) r_j^{(\alpha)}] \tag{3.95}$$

Operating a shift of the origin, it can be shown that the expression of the magnetic dipole has no differences with respect to the spinless case, viceversa in the expression of the magnetic quadrupole moment appear an additional term explicitly dependent on the spin operator. Therefore, the expressions of the tensors H_{ijk} and H'_{ijk} are modified, since they are the only polarizabilities that depend from the matrix elements of the magnetic quadrupole moment. However, the spinless definitions of the multipole moment operators used to derive a frequency-independent expression of the magnetizability are still valid and reliable, in the hypothesis to work with closed-shell, and so it is simpler to neglect the spin terms.

Chapter 4

Magnetizability in a relativistic framework

In this chapter I will derive and discuss the magnetizability in the relativistic framework, pointing out the differences with the non-relativistic approach considered so far.
Let start looking at the interaction of a single particle with an external electromagnetic field, described by the Dirac Hamiltonian:

$$H_D = \beta mc^2 + c(\boldsymbol{\alpha} \cdot \boldsymbol{p}) + ec(\boldsymbol{\alpha} \cdot \boldsymbol{A}) - e\phi \tag{4.1}$$

Comparing this expression with the non-relativistic Hamiltonian used in the previous chapter, we can recognize that no quadratic term in the vector potential appear in the relativistic Hamiltonian, whereas the non-relativistic Hamiltonian include both linear and quadratic terms in $\boldsymbol{A}$. Thus, when the second-order perturbation in the energy is computed using perturbation theory, only one term in the vector potential will contribute, namely:

$$E_{(2)} = \sum_{n \neq 0} \frac{< 0 \mid ec(\boldsymbol{\alpha} \cdot \boldsymbol{A}) \mid n >< n \mid ec(\boldsymbol{\alpha} \cdot \boldsymbol{A}) \mid 0 >}{E_0 - E_n} \tag{4.2}$$

where $\mid n >$ is a 4-component wave function. Referring to the previous analysis, it is possible to state that the diamagnetic term does not appear in the relativistic case, and therefore the expression of the magnetizability contains only the contribution given by the paramagnetic term. However, the diamagnetic term can be recovered in the non-relativistic limit, using perturbation theory and including positronic states[9].
It is important to note that the magnetic moments are differently defined in the relativistic and in the non-relativistic domain. A standard way to derive the expressions for the magnetic moments is to insert the expansions

of the vector and of the scalar potentials (1.21)-(1.22), given by the multipole gauge, in the corresponding Hamiltonians (2.8) and (2.15), in order to have the Hamiltonians written in terms of electric and magnetic multipoles. Thus, the non-relativistic magnetic moments, in the most general way, can be defined as:

$$
\begin{aligned}
\boldsymbol{m}^{[n]}_{j_1,\ldots,j_{n-1}} = & -\frac{e}{2m}(\frac{n}{n+1})\{(r_{j_1}\ldots r_{j_{n-1}})\boldsymbol{l}+\boldsymbol{l}(r_{j_1}\ldots r_{j_{n-1}})\} \\
& -\frac{e}{2m}(\frac{n}{n+1})(r_{j_1}\ldots r_{j_{n-1}})(\boldsymbol{r}\wedge e\boldsymbol{A}) \\
& -\frac{e}{2m}(\frac{n}{n+1})\{(r_{j_1}\ldots r_{j_{n-1}})(\boldsymbol{r}\cdot\boldsymbol{\sigma})\nabla \\
& +\nabla(\boldsymbol{\sigma}\cdot\boldsymbol{r})(r_{j_1}\ldots r_{j_{n-1}})\} \\
& +\frac{e}{2m}(\frac{n}{n+1})\boldsymbol{\sigma}\{(r_{j_1}\ldots r_{j_{n-1}})(\boldsymbol{r}\cdot\nabla) \\
& +(\nabla\cdot\boldsymbol{r})(r_{j_1}\ldots r_{j_{n-1}})\}
\end{aligned}
\tag{4.3}
$$

In particular, the magnetic dipole and the magnetic quadrupole moments are:

$$
\boldsymbol{m}^{[1]} = -\frac{e}{2m}(\boldsymbol{l}+\boldsymbol{\sigma})-\frac{e^2}{4m}(\boldsymbol{r}\wedge\boldsymbol{A})
\tag{4.4}
$$

$$
\boldsymbol{m}^{[2]}_k = -\frac{e}{2m}[r_k(\frac{2}{3}\boldsymbol{l}+\boldsymbol{\sigma})+(\frac{2}{3}\boldsymbol{l}+\boldsymbol{\sigma})r_k]+\frac{e}{3m}(\boldsymbol{\sigma}\cdot\boldsymbol{r})_k-\frac{e}{3m}r_k(\boldsymbol{r}\wedge e\boldsymbol{A})
\tag{4.5}
$$

Note that the expressions of the magnetic moments derived in the non-relativistic framework are cumbersome, given the presence of spin-dependent terms. Viceversa, much more simple definitions of the magnetic moments are obtained in the relativistic case:

$$
\boldsymbol{m}^{[n]}_{j_1,\ldots,j_{n-1}} = -ec(\frac{n}{n+1})r_{j_1}\ldots r_{j_{n-1}}(\boldsymbol{r}\wedge\boldsymbol{\alpha})
\tag{4.6}
$$

and so the relativistic magnetic dipole and quadrupole moments are:

$$
m^{[1]}_i = -\frac{1}{2}ec(\mathbf{r}\wedge\boldsymbol{\alpha})_i = \frac{1}{2}(\boldsymbol{r}\wedge\boldsymbol{j})_i
\tag{4.7}
$$

$$
m^{[2]}_{ij} = -\frac{2}{3}ecr_i(\mathbf{r}\wedge\boldsymbol{\alpha})_j = \frac{2}{3}r_i(\boldsymbol{r}\wedge\boldsymbol{j})_j
\tag{4.8}
$$

where $\boldsymbol{\alpha}$ is the Dirac matrix and $\boldsymbol{j}$ is the relativistic current density, introduced in section 2.2, in terms of which it is possible to define the magnetic moments.

Looking at the relativistic expressions of the Hamiltonian and of the magnetic moments, it appears convenient work at the relativistic level, if not for the fact that transition moments are calculated in terms of 4-component spinors, which are eigenvectors of the Dirac Hamiltonian, and so the formalism turns out to be pretty cumbersome.

It is useful to study the magnetizability in the relativistic framework writing its expression in the form:

$$\chi_{\imath\jmath} = \ll m_\imath ; m_l \gg_\omega = \ll \frac{1}{2}(\boldsymbol{r} \wedge c\boldsymbol{\alpha})_\imath ; \frac{1}{2}(\boldsymbol{r} \wedge c\boldsymbol{\alpha})_l \gg_\omega \tag{4.9}$$

where response theory and the Heisenberg relation $-\frac{\imath\hbar}{m}[\boldsymbol{r}, H] = c\boldsymbol{\alpha}$ have been used.

In order to analyze the origin-dependence of the magnetizability, let us apply a shift $\boldsymbol{d}$ of the position operator $\boldsymbol{r}$, as previously done in Chapter 3: $\boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{d}$. Thus, after a displacement of the origin of the coordinates, the expression for the magnetizability shows three additional terms:

$$\begin{aligned} \chi'_{\imath\jmath} \;=\; & \ll \frac{1}{2}(\boldsymbol{r} \wedge c\boldsymbol{\alpha})_\imath ; \frac{1}{2}(\boldsymbol{r} \wedge c\boldsymbol{\alpha})_l \gg_\omega \\ & - \frac{i}{2}\hbar\omega\varepsilon_{\imath\jmath k} d_\jmath \ll r_k ; \frac{1}{2}\left(\boldsymbol{r} \times c\boldsymbol{\alpha}\right)_l \gg_\omega \\ & - \frac{i}{2}\hbar\omega\varepsilon_{l\jmath k} d_\jmath \ll \frac{1}{2}\left(\boldsymbol{r} \times c\boldsymbol{\alpha}\right)_i ; r_k \gg_\omega \\ & - \frac{1}{4}\varepsilon_{\imath\jmath k}\varepsilon_{lmn} d_\jmath d_m \hbar^2\omega^2 \ll r_k ; r_n \gg_\omega \end{aligned} \tag{4.10}$$

Note that the displacement obtained here is analogues to the expression derived in the non-relativistic framework, eq. (3.62), where two linear and one quadratic term in $\boldsymbol{d}$ appear. This is not surprising, since the diamagnetic part of the magnetizability is always frequency-independent, and it does not show up in the relativistic framework[1].

I emphasize that an important difference between the relativistic and the non-relativistic case to keep in mind is the definition of the magnetic moments.

4.1 Frequency-independent magnetizability

Let consider the case of an external, homogeneous, static magnetic field. Looking at the expression for the magnetizability after the displacement (4.10), it is clear that for $\omega = 0$, the three additional terms go to zero,

---

[1] As mentioned before, it is possible to recover the diamagnetic term in the non-relativistic limit, using perturbation theory and including positronic states.

therefore the magnetizability is an origin-independent quantity when a static magnetic field is considered, as it has been obtained in the non-relativistic framework.
Note, that here it is not possible to apply the procedure introduced by Van Vleck to demonstrate the origin independence of the magnetizability. In fact, as already underlined, the relativistic Hamiltonian contains only the linear term in the vector potential, so the expression for the magnetizability has only the paramagnetic term in it, and therefore no mutual cancellation between the paramagnetic and the diamagnetic terms can occur. Furthermore, it is not possible to rewrite the relativistic magnetic moments in terms of the angular momentum, and so reduce the paramagnetic and the diamagnetic contributions to the same form, since the different definitions of the magnetic moments in the two frameworks. Thus, multipole theory provides the best framework to infer the origin independence of the static magnetizability.
Despite the differences just mentioned between the relativistic and the non-relativistic case, it is possible to generally state that the magnetizability is an origin-independent quantity when an external static magnetic field is applied.

4.2 Frequency-dependent magnetizability

The origin dependence of the frequency-dependent magnetizability in the non-relativistic case has been discussed in detail in Chapter 3, and an origin-independent expression has been obtained following the idea of Raab and de Lange (3.91). As already mentioned, I do not consider this quantity as the magnetizability, but more generally as a second-order magnetic property, given that it is a collection of several terms, and it does not include only the magnetic dipole-magnetic dipole contribution.
Now I will focus my analysis on the relativistic expression for the magnetizability eq. (4.9), with particular attention to the additional terms obtained after a displacement of the origin of the coordinates, eq. (4.10). Let us discuss in detail these displacement terms. The linear terms in $\boldsymbol{d}$ have the same form, except for the indices:

$$\begin{aligned}(4.11)\qquad & -\frac{i}{2}\hbar\omega\varepsilon_{\imath\jmath k}d_\jmath \ll r_k; \frac{1}{2}\left(\boldsymbol{r}\times c\boldsymbol{\alpha}\right)_l \gg_\omega \\ & -\frac{i}{2}\hbar\omega\varepsilon_{l\jmath k}d_\jmath \ll \frac{1}{2}\left(\boldsymbol{r}\times c\boldsymbol{\alpha}\right)_i; r_k \gg_\omega\end{aligned}$$

Not all of these indices are dumb indices (following Einstein's summation rule), therefore it is not possible to sum the two contributions, but it is necessary to consider them separately. Note that the response function is given by the electric dipole operator together with the magnetic dipole operator. According to the definition of the polarizabilities given in chapter 3, it is possible to claim that the linear terms in the displacement are proportional to the G_{ij} tensor. The quadratic term in $\boldsymbol{d}$ contains the electric dipole-electric dipole contribution, thus it can be considered proportional to the polarizability tensor α_{ij}. A comparison with the displacement terms obtained in section 3.3 shows that the same additional terms appear in both relativistic and non-relativistic cases. Again, we have to keep in mind that the magnetic dipole moments have different definitions in the two frameworks.

In order to obtain an origin-independent expression of the magnetizability, the additional terms that occur after a shift of the origin have to be zero, or have to be cancelled introducing other identical polarizabilities with opposite sign.

I have considered several symmetric configurations of a molecule, discussing the possibility that for a specific symmetry the G_{ij}-tensors and the α_{ij}-tensor could have been zero. It is possible to infer that no specific symmetry leave both tensors equal to zero. Even considering a simple spherical symmetry, it is well known that the G_{ij}-tensors go to zero, but not the polarizability α_{ij}[31]. Thus, the symmetry of a molecule do not help to solve the problem of the origin dependence of the magnetizability.

4.2.1 The role of the electric quadrupole

Origin-independent expressions of various molecular properties have been derived as sum of different polarizabilities. Important examples are optical rotation and circular dichroism, which are described by a linear combination of the tensors a_{ijk} and G_{ij}[31]:

$$\xi'_{ijk} = -\frac{1}{c}[\frac{1}{3}\omega(a_{i,jk} - a_{j,ik}) + G'_{ii} + G'_{jj}] \tag{4.12}$$

I have already mentioned that the tensors a_{ijk} and G_{ij} are origin dependent in the presence of a frequency-dependent electromagnetic field, however, their linear combination in eq. (4.12) is such that the ξ'_{ijk} resulting is origin-independent. Since ξ'_{ijk} describe observable quantities, as optical rotation and circular dichroism, its expression has to be origin-independent, and so this requirement is fulfilled by the linear combination of the polarizabilities a_{ijk} and G_{ij}. Thus, it is reasonable to consider the possibility of deriving an origin-independent expression of a molecular property as a linear combination of different polarizabilities. It is also important to note that optical rotation and circular dichroism have electric dipole-magnetic dipole and electric dipole-electric quadrupole contributions, contained in the tensors $G_{\imath\jmath}$ and $a_{\imath\jmath k}$ respectively.

In the light of this analysis, I have tried to obtain an origin-independent expression of the magnetizability as a linear combination of polarizabilities. By definition, the magnetizability contains the magnetic dipole-magnetic dipole contribution only, and its expression is origin dependent for a frequency-dependent magnetic field. Thus, the idea is to add to the magnetic dipole-magnetic dipole term also a magnetic dipole-electric quadrupole contribution, exactly as it has been done for the optical rotation, in order to obtain a linear combination of polarizabilities that give an origin-independent expression for this second-order magnetic property[2]. This approach is supported by the fact that I am working using a multipole expansion of the vector potential, therefore the order of the multipole moments in the expansion is such that the magnetic dipole has to be considered together with the electric quadrupole, given that they appear at the same order in the fields[7].

The expression that I have been considered has the form:

$$\chi_{\imath l} = \ll m_\imath + \frac{1}{2}\imath\hbar\omega\varepsilon_{\imath\jmath k}q_{\jmath k}; m_l + \frac{1}{2}\imath\hbar\omega\varepsilon_{lmn}q_{mn} \gg \tag{4.13}$$

where in the response function I have added to the magnetic dipole also the electric quadrupole moment $q_{\imath\jmath}$. The electric quadrupole tensor has to be contracted with the antisymmetric tensor $\varepsilon_{\imath\jmath k}$, in order to be consistent with the grade and the symmetries of the magnetic dipole moment. Furthermore, eq. (4.13) contain a numerical factor, $\hbar$ and the frequency of the external field ω, consistent with the optical rotation analysis and with the units.

Following a standard procedure, it is possible to operate a shift of the origin of the coordinates, and check if the alternative expression of the second-order magnetic property, introduced in eq. (4.13), is origin-independent. As before, I consider a displacement $\boldsymbol{d}$, such that the position operator in the definition of the multipole moments is redefined as: $\boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{d}$. The calculus is simple but pretty cumbersome, and lead to an expression made of 36 terms. 4 of them are obviously the same terms resulting from the magnetic dipole-magnetic dipole coupling, instead the other 32 are given by the couplings of the magnetic dipole-electric quadrupole and electric quadrupole-electric quadrupole moments. The resulting expression of the second-order magnetic

---

[2] For the reasons highlighted before, I will not call this quantity magnetizability anymore, since now its expression has several contributions from different polarizabilities.

response, after a shift of the origin of the coordinates, is:

$$
\begin{aligned}
\chi'_{\imath l} \quad = \quad & \chi_{\imath l} - \frac{\imath}{2}\hbar\omega\varepsilon_{lrs}d_r \ll m_\imath ; q_s \gg \\
& - \frac{\imath}{2}\hbar\omega\varepsilon_{\imath pq}d_p \ll q_q ; m_l \gg \\
& - \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath pq}\varepsilon_{lrs}d_p d_r \ll q_q ; q_s \gg \\
& + \frac{\imath}{2}\hbar\omega\varepsilon_{\imath\jmath k} \ll q_{\jmath k} ; m_l \gg \\
& + \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lrs}d_r \ll q_{\jmath k} ; q_s \gg \\
& + \frac{\imath}{2}\hbar\omega\varepsilon_{\imath\jmath k}d_k \ll q_\jmath ; m_l \gg \\
& + \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lrs}d_k d_r \ll q_\jmath ; q_s \gg \\
& + \frac{\imath}{2}\hbar\omega\varepsilon_{\imath\jmath k}d_\jmath \ll q_k ; m_l \gg \\
& + \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lrs}d_j d_r \ll q_k ; q_s \gg \\
& + \frac{\imath}{2}\hbar\omega\varepsilon_{lmn} \ll m_\imath ; q_{mn} \gg \\
& + \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath pq}\varepsilon_{lmn}d_p \ll q_q ; q_{mn} \gg \\
& + \frac{\imath}{2}\hbar\omega\varepsilon_{lnm}d_n \ll m_\imath ; q_m \gg \\
& + \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath pq}\varepsilon_{lmn}d_p d_n \ll q_q ; q_m \gg \\
& + \frac{\imath}{2}\hbar\omega\varepsilon_{lmn}d_m \ll m_\imath ; q_n \gg \\
& + \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath pq}\varepsilon_{lmn}d_p d_m \ll q_q ; q_n \gg \\
& - \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lmn} \ll q_{\jmath k} ; q_{mn} \gg \\
& - \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lmn}d_n \ll q_{\jmath k} ; q_m \gg \\
& - \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lmn}d_m \ll q_{\jmath k} ; q_n \gg \\
& - \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lmn}d_k \ll q_\jmath ; q_{mn} \gg \\
& - \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lmn}d_k d_n \ll q_\jmath ; q_m \gg \\
& - \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lmn}d_k d_m \ll q_\jmath ; q_n \gg \\
& - \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lmn}d_\jmath \ll q_k ; q_{mn} \gg \\
& - \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lmn}d_j d_n \ll q_k ; q_m \gg \\
& - \frac{1}{4}\hbar^2\omega^2\varepsilon_{\imath\jmath k}\varepsilon_{lmn}d_j d_m \ll q_k ; q_n \gg
\end{aligned}
\tag{4.14}
$$

where the terms which contain only the displacement $\boldsymbol{d}$ in the response functions have been omitted, given that they are obviously zero. Looking at eq. (4.14), it is possible to note that several polarizabilities appear, namely: $G'_{ijk}, \alpha_{ij}, a_{ijk}, L'_{jkl}, d_{ijkl}$, following the notation introduced in chapter 3. The definition of the second-order magnetic property obtained here includes the magnetic dipole-magnetic dipole contribution plus three further terms, two given by the magnetic dipole-electric quadrupole coupling, and one given by the electric quadrupole-electric quadrupole coupling. All the other terms are linear or quadratic in the displacement $\boldsymbol{d}$, therefore I would expect that they delete each other, avoiding any dependence on the choice of the origin. An analysis of the terms that appear in eq. (4.14) leads to the conclusion that: include the electric quadrupole moment in the definition of the second-order magnetic response do note solve the problem of origin-dependence, since its expression is still origin-dependent when a frequency-dependent magnetic field is applied. In fact, there is no possible way to change and switch the index of the tensors in eq. (4.14) in order to cancel the displacement terms, and furthermore there is an odd number of the α_{ij} polarizability tensor, quadratic in the displacement, that cannot be eliminated.

4.3 Remarks

No origin-independent expression of the frequency-dependent magnetizability has been found in the relativistic domain. The idea to include the electric quadrupole contribution in the definition of the second-order magnetic response is definitely suitable, in agreement with the previous discussion and considering the multipole expansion of the vector potential, but it does not lead to any origin-independent expression. However, by virtue of the considerations done so far, I still believe that the electric quadrupole contribution has to be considered when we are treating magnetic properties, and that the relativistic framework is the proper domain in which to work, in order to have physical-acceptable results. In particular, I think that a deeper analysis of the relativistic Hamiltonian, of the expansion of the potentials, and of the gauge functions could lead to an origin-independent expression of the second-order magnetic response. There are also no doubts that it is easier to work in the relativistic domain, as long as no calculation are performed[3], since the relativistic Hamiltonian has only a linear term in the vector potential.

Note that it would be possible to consider one order higher in the multipole expansion, thus to include the electric octopole-magnetic quadrupole contri-

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[3] Relativistic calculation are more difficult compared to the non-relativistic one, since 4-components wave functions have to be considered.

bution in the definition of the second-order magnetic response, as done by Raab and de Lange in the non-relativistic domain and discussed in Chapter 3. However, as I have already stated, I think that the procedure used by Raab and de Lange to obtain an origin-independent expression for the magnetizability is quite artificial, and it gives no information about the quantum-mechanical origin of their final result, since no modification of the non-relativistic Hamiltonian has been done, and their origin-independent expression does not come naturally from the multipole approach, but it has been built collecting several polarizabilities. Thus, even if a similar approach could be applied to the relativistic framework, I will not discuss it. It is important to remark that the inclusion of the electric quadrupole moment in the definition of the second-order magnetic response is motivated by the fact that it appears at the same order of the magnetic dipole in the multipole expansion of the vector and scalar potentials, therefore neglect the electric quadrupole contribution would not be consistent with multipole theory.

I would like to point out once more that the electromagnetic fields are described by the Maxwell equations, which are fully relativistic. In the next chapter I will consider the macroscopic Maxwell equations, and referring to the work of Raab and de Lange[8], I will derive origin-independent expressions of the material constants. The results that I will discuss in the macroscopic case can be considered a good starting point to obtain origin-independent expressions of second-order magnetic properties in the microscopic case too. In fact, no specific hypothesis will be done, but only the non-unique definition of the response fields will be used, within a fully relativistic discussion.

Chapter 5

Macroscopic analysis

5.1 Macroscopic Maxwell equations and response fields

So far, my work has been focused on the analysis of second-order magnetic response, using a microscopic description of a physical system. The discussion has been based on the microscopic Maxwell equations, introduced in chapter 1, and it represents a good approach, in order to treat molecular properties for a charge distribution. However, it is possible to extend the description to the macroscopic case, and study the multipole moments induced in bulk matter. A standard approach consist of taking the spatial average at a certain time of the expectation values of the microscopic multipole moments, and introducing the macroscopic multipole moment densities. The procedure used to obtain the definition of the macroscopic multipole moment densities, starting from the multipole expansion of the potentials, is well known from the literature, e.g.[1]. Here, I would like to point out that when the average of the vector and of the scalar potentials is performed, further terms in the definition of the current and charge densities appear naturally. In fact, given that a bulk of matter of finite dimension is considered, surface effects emerge, namely bound charge density and bound current density. These quantities are included in the macroscopic Maxwell equations together with the averaged free sources densities. Let so define the macroscopic Maxwell equations and discuss the physical quantities that appear in them, where the fields and the sources are averaged in space, at a fixed time:

$$\nabla \cdot \boldsymbol{E} = \frac{1}{\varepsilon_0}(\rho_f + \rho_b) \tag{5.1}$$

$$\nabla \wedge \boldsymbol{B} = \mu_0(\boldsymbol{J}_f + \boldsymbol{J}_b + \varepsilon_0 \frac{\partial \boldsymbol{E}}{\partial t}) \tag{5.2}$$

$$\nabla \wedge \boldsymbol{E} + \frac{\partial B}{\partial t} = 0 \tag{5.3}$$

$$\nabla \cdot \boldsymbol{B} = 0 \tag{5.4}$$

ρ_f and $\boldsymbol{J}_f$ are the free source charge and current densities , while ρ_b and $\boldsymbol{J}_b$ are the bound charge and current densities that occur when the surface effects in the medium are considered. The definitions of ρ_b and $\boldsymbol{J}_b$ are obtained from the expansion of the vector and of the scalar potentials, thus it is possible to write their expressions in terms of multipole moments[1]:

$$\nabla_\imath(\varepsilon_0 E_\imath + P_i - \frac{1}{2}\nabla_j Q_{\imath\jmath} + \frac{1}{6}\nabla_k \nabla_j Q_{\imath\jmath k} + \ldots) = \rho_f \tag{5.5}$$

$$\begin{aligned} &\varepsilon_{\imath\jmath k}\nabla_j(\frac{1}{\mu_0}B_\imath - M_i + \frac{1}{2}\nabla_j M_{\imath\jmath} + \ldots) = \\ &= J_{f\imath} + \varepsilon_0 \frac{\partial E_\imath}{\partial t} + \frac{\partial P_i}{\partial t} - \frac{1}{2}\nabla_j \frac{\partial Q_{\imath\jmath}}{\partial t} + \frac{1}{6}\nabla_k \nabla_j \frac{\partial Q_{\imath\jmath k}}{\partial t} + \ldots \end{aligned} \tag{5.6}$$

The macroscopic multipole moment densities are labelled with capital letters ($P_\imath$, $Q_{\imath\jmath}$, $M_\imath$...), and their expressions are obtained averaging the microscopic definitions of the multipole moments. Inserting eqs. (5.5) and (5.6) in the macroscopic Maxwell equations, the quantities $\boldsymbol{D}$ and $\boldsymbol{H}$ can be defined:

$$D_\imath = \varepsilon_0 E_\imath + P_i - \frac{1}{2}\nabla_j Q_{\imath\jmath} + \frac{1}{6}\nabla_k \nabla_j Q_{\imath\jmath k} + \ldots \tag{5.7}$$

$$H_\imath = \frac{1}{\mu_0}B_\imath - M_i + \frac{1}{2}\nabla_j M_{\imath\jmath} + \ldots \tag{5.8}$$

$\boldsymbol{D}$ and $\boldsymbol{H}$ are termed macroscopic response fields. In fact, the multipole moment densities that appear in the previous definitions include induced contributions, which result from the response of the matter to the applied fields. Note, that the procedure used to move from the microscopic to the macroscopic cases takes the average of the fields and of the multipole moments, on a scale where the variation of these quantities is small compared to the molecular dimension. Furthermore, the expansions of the response fields are truncated at the electric octopole-magnetic quadrupole order, so again it is necessary to include multipole contributions of comparable magnitude, according with the hierarchy (order) in the expansion of the vector and of the scalar potentials.

In terms of the response fields, the macroscopic, inhomogeneous Maxwell equations are:

$$\nabla \cdot \boldsymbol{D} = \rho_f \tag{5.9}$$

$$\nabla \wedge \boldsymbol{H} = \boldsymbol{J}_f + \frac{\partial \boldsymbol{D}}{\partial t} \tag{5.10}$$

5.2 Material constants

In order to apply the Maxwell equations using the formulation in terms of free/bound charge and current and response fields, it is necessary to specify the relations between $\boldsymbol{D}$ and $\boldsymbol{E}$, and $\boldsymbol{H}$ and $\boldsymbol{B}$. Finding relations between these fields means that to solve Maxwell equations by employing the free/bound partition of charges and currents, one needs the properties of the materials relating the response of bound currents and bound charges to the fields applied to these materials. The material properties specifying the response of bound charges and currents to the field are called constitutive relations, and correspond physically to how much polarization and magnetization a material acquires in the presence of electromagnetic fields.

In the absence of magnetic or dielectric materials, the constitutive relations are simple:

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} \quad ; \quad \boldsymbol{H} = \frac{1}{\mu_0}\boldsymbol{B} \tag{5.11}$$

where ε_0 and μ_0 are the permittivity of free space and the permeability of free space, respectively. In a linear, isotropic, non-dispersive, uniform material, the relations are similar:

$$\boldsymbol{D} = \varepsilon \boldsymbol{E} \quad ; \quad \boldsymbol{H} = \frac{1}{\mu}\boldsymbol{B} \tag{5.12}$$

Here ε and μ are constants depending on the material, which are called permittivity and permeability of the material, respectively.

In the general case, the constitutive relations are not simple proportionalities. The relations can usually still be written as in eq. (5.12), but now ε and μ are not simple constants, but rather functions that can depend on the strength, the direction, and the frequency of the electric and magnetic fields. Other dependencies can occur for non-uniform or ferromagnetic materials.

According to the definition given in eqs. (5.7) and (5.8) of the response fields, up to the electric octopole-magnetic quadrupole order, we can see that the constitutive relations take a more complicated form. Let us now derive the constitutive relations at this order, in terms of the macroscopic polarizabilities.

In chapter 3, definitions of the polarizabilities have been obtained in the microscopic case using perturbation theory. As already mentioned, these definitions can be extended to the macroscopic case performing a spatial average of the multipole moments involved in them. Thus, recalling the expressions of the multipole moments, and operating a spatial average in order to have the multipole moment densities, it is possible write the response fields $\boldsymbol{D}$ and $\boldsymbol{H}$ in terms of the macroscopic polarizabilities. In particular, considering a specific case where the external fields $\boldsymbol{E}$ and $\boldsymbol{B}$ are represented by harmonic plane waves, eqs. (5.7) and (5.8) assume the form:

$$D_\imath = A_{\imath\jmath}E_\jmath + T_{\imath\jmath}B_\jmath \tag{5.13}$$

$$H_\imath = U_{\imath\jmath}E_\jmath + X_{\imath\jmath}B_\jmath \tag{5.14}$$

for the response fields, where the second-rank tensors $A_{\imath\jmath}$, $T_{\imath\jmath}$, $U_{\imath\jmath}$ and $X_{\imath\jmath}$ have been introduced and they are named material constants. Their expressions in terms of the macroscopic polarizabilities are:

$$\begin{aligned} A_{\imath\jmath} \;=\;& \varepsilon_0\delta_{\imath\jmath} + \alpha_{\imath\jmath} - \imath\alpha'_{\imath\jmath} + \frac{1}{2}[\imath(a_{\imath\jmath k} - a_{\jmath k\imath}) + a'_{\imath\jmath k} + a'_{\jmath k\imath}]k_k \\ & + [-\frac{1}{6}(b_{\imath\jmath kl} + b_{\jmath\imath kl}) + \frac{\imath}{6}(b'_{\imath\jmath kl} - b'_{\jmath\imath kl}) \\ & - \frac{1}{4}(d_{\imath k\jmath l} - \imath d'_{\imath k\jmath l})]k_k k_l \end{aligned} \tag{5.15}$$

$$T_{\imath\jmath} = G_{\imath\jmath} - \imath G'_{\imath\jmath} + \frac{1}{2}[\imath(H_{\imath\jmath k} - L_{\imath k\jmath}) + H'_{\imath\jmath k} - L'_{\imath k\jmath}]k_k \tag{5.16}$$

$$U_{\imath\jmath} = -G_{\jmath\imath} - \imath G'_{\jmath\imath} + \frac{1}{2}[\imath(H_{\jmath\imath k} - L_{\jmath k\imath}) - H'_{\jmath\imath k} + L'_{\jmath k\imath}]k_k \tag{5.17}$$

$$X_{\imath\jmath} = \frac{1}{\mu_0}\delta_{\imath\jmath} - \chi_{\imath\jmath} + \imath\chi'_{\imath\jmath} \tag{5.18}$$

where the permanent multipole densities have been omitted, and $\boldsymbol{k}$ is the wave vector present in the definition of the harmonic plane waves. Note that for homogeneous mediums, the latter tensor gives no contributions to the

Maxwell equations, and that for non-magnetic mediums, some of the contributions included in the previous expressions vanish.
Here, I am restricting the analysis to non-dissipative media, however the following discussion can be extended and it is still valid for dissipative media[1].
The material constants represent physical observables: A_{ij} the permittivity, T_{ij} and U_{ij} the magnetoelectric effects, and X_{ij} the inverse permeability, therefore they are supposed to be origin-independent quantities. Operating a shift of the origin of the coordinates, and recalling the displacement terms introduced in section 3.3, it is straightforward to state that the expressions of the material constants, obtained using multipole theory up to the electric octopole-magnetic quadrupole order, are origin dependent, for both non-magnetic and magnetic materials. In particular, the displacement terms of the macroscopic polarizabilities that appear in the expressions of the material constants, in the general case of a magnetic material, have been defined in eqs. (3.48)-(3.63)[2].
Obviously, the definitions of the material constants obtained using multipole theory are not physically acceptable, thus it is natural look for origin-independent expressions. One possible way to work on this issue is to exploit the non-unicity of the response fields and of the material constants. Let analyze in detail these aspects.

5.3 Transformation theory

In chapter 1 I have been discuss the microscopic Maxwell equations and the non-unicity of the vector and of the scalar potentials, which are completely defined only when a particular choice of gauge is done. A similar situation occur considering the inhomogeneous macroscopic Maxwell equations (5.9) and (5.10), in fact, referring again to the Helmholtz's theorem[10], a freedom in the definitions of the response fields $\boldsymbol{D}$ and $\boldsymbol{H}$ can be inferred. Clearly, the inhomogeneous macroscopic Maxwell equations have to be valid for any possible choice of the response fields, thus, when a transformation on $\boldsymbol{D}$ and $\boldsymbol{H}$ is performed, it is important to consider the possible changes in the external fields $\boldsymbol{E}$ and $\boldsymbol{B}$ and in the constitutive relations.

---

[1] Note that, for dissipative media, all the polarizability tensors and the wave vectors in the expressions of the material constants are complex quantities.

[2] Again, we have to keep in mind that the results obtained in chapter 3 were derived in the microscopic case, so the corresponding expressions for the macroscopic case are obtained averaging the microscopic definitions in space.

At first, let consider a transformation of the response fields of the form:

$$
\begin{aligned}
D_\imath &\rightarrow D_\imath - \frac{1}{\omega}\varepsilon_{\imath\jmath k} k_\jmath H_k^G \\
H_\imath &\rightarrow H_\imath + H_\imath^G
\end{aligned}
\tag{5.19}
$$

I will refer to eq. (5.20) as "gauge transformations"[7], although they are different from the gauge transformations previously introduced. It is convenient to derive these transformations, considering the Fourier expansions of the response fields and of the current and charge free source densities. Substituting these Fourier expansions in the Fourier transform of the inhomogeneous Maxwell equations, we are lead to the transformations:

$$
\begin{aligned}
\boldsymbol{D}(\boldsymbol{k},\omega) &\rightarrow \boldsymbol{D}(\boldsymbol{k},\omega) - \frac{1}{\omega}\boldsymbol{k} \wedge \boldsymbol{H}^G(\boldsymbol{k},\omega) \\
\boldsymbol{H}(\boldsymbol{k},\omega) &\rightarrow \boldsymbol{H}(\boldsymbol{k},\omega) + \boldsymbol{H}^G(\boldsymbol{k},\omega)
\end{aligned}
\tag{5.20}
$$

valid for an arbitrary choice of $\boldsymbol{H}^G$. Here $\boldsymbol{k}$ is the wave vector and ω the frequency of the fields. Considering fields represented by harmonic plane waves, and if $\boldsymbol{H}^G(\boldsymbol{r},t)$ is a complex harmonic plane wave too, it is possible to derive eq. (5.20) in terms of the fields. Note that these gauge transformations change the response fields $\boldsymbol{D}$ and $\boldsymbol{H}$, but do not alter the relative contributions of $\boldsymbol{E}$ and $\boldsymbol{B}$ to $\boldsymbol{D}$ and $\boldsymbol{H}$. They therefore do not imply any changes in the material constants.

An opposite situation occurs for another set of transformations, known as "Faraday's transformations", where the response fields are unchanged, but the relative contributions of $\boldsymbol{E}$ and $\boldsymbol{B}$ to $\boldsymbol{D}$ and $\boldsymbol{H}$ are modified, thus a change in the material constants have to be considered in order to not alter the response fields. Faraday's transformations are defined as

$$
\begin{aligned}
D_\imath &\rightarrow D_\imath + D_\imath^F \\
H_\imath &\rightarrow H_\imath + H_\imath^F
\end{aligned}
\tag{5.21}
$$

where, for any second-rank tensors $Z_{\imath\jmath}^F$ and $Y_{\imath\jmath}^F$, $D_\imath^F$ and $H_\imath^F$ are:

$$
\begin{aligned}
D_\imath^F &= Z_{\imath\jmath}^F(B_\jmath - \frac{1}{\omega}\varepsilon_{\jmath mn} k_m E_n) \\
H_\imath^F &= Y_{\imath\jmath}^F(B_\jmath - \frac{1}{\omega}\varepsilon_{\jmath mn} k_m E_n)
\end{aligned}
\tag{5.22}
$$

These transformations are based on one of the homogeneous Maxwell equations, namely Faraday's law, eq. (1.2), which for complex harmonic fields can be written as:

$$
\varepsilon_{\jmath mn} k_m E_n - \omega B_\jmath = 0
\tag{5.23}
$$

confirming that, by construction, Faraday's transformations do not change the response fields $\boldsymbol{D}$ and $\boldsymbol{H}$. Note that the second-rank tensors $Z^F_{\imath\jmath}$ and $Y^F_{\imath\jmath}$ have to satisfy specific requirements, in order to be consistent with the discussion above, vide infra.

5.4 Origin-independent material constants

The idea now is to derive origin-independent expressions of the material constants, starting from the definitions obtained in multipole theory, and using the two sets of transformations just introduced. In the analysis it is necessary and useful to fix some constraints, consistent with the fact that the discussion is based on multipole theory. Thus, when the gauge and Faraday's transformations are applied, the linearity of the relations between the response fields $\boldsymbol{D}$ and $\boldsymbol{H}$ with the fields $\boldsymbol{E}$ and $\boldsymbol{B}$ and the macroscopic polarizabilities have to be preserved[3], as well as the space and time symmetries of the polarizability tensors[31], and the order of the multipole moments in the multipole expansions[4].

The material constants, defined by the tensors introduced in equations (5.15)-(5.18), possess intrinsic symmetries; in particular, considering a non-dissipative medium, we have:

$$\begin{aligned} A_{\imath\jmath} &= A^*_{\jmath\imath} \\ U_{\imath\jmath} &= -T^*_{\jmath\imath} \\ X_{\imath\jmath} &= X^*_{\jmath\imath} \end{aligned} \tag{5.24}$$

These relations have been obtained using the Lagrangian formulation of classical field theory in macroscopic electromagnetism, deriving the Lagrangian density in terms of the response fields, and exploiting the fact that it is a real function of these quantities and unique in terms of the external fields $\boldsymbol{E}$ and $\boldsymbol{B}$[7].

Considering the linear constitutive relations in covariant form, one more symmetry relation for the magnetoelectric constants has been derived, known as the Post constraint[32]:

$$T_{\imath\imath} = U_{\imath\imath} \tag{5.25}$$

The Post constraint does not involve dielectric or purely magnetic properties, and it will not be used further in this work.

---

[3] Recall that I have assumed harmonic plane waves for the fields.

[4] The electric quadrupole has to appear together with the magnetic dipole, the electric octopole with the magnetic quadrupole etc., as I have already mentioned before.

Let list the constraints and the comments introduced so far, in order to derive origin-independent expressions of the material constants, using the gauge and Faraday's transformations:

1. The gauge transformations act on the response fields $\boldsymbol{D}$ and $\boldsymbol{H}$, and therefore they change the material constants too, while Faraday's transformations only modify the constitutive tensors.
2. The linear homogeneous dependence of the response fields $\boldsymbol{D}$ and $\boldsymbol{H}$ on the fields $\boldsymbol{E}$ and $\boldsymbol{B}$ and on the macroscopic polarizability tensors has to be preserved.
3. The order in the multipole expansions has to be consistent with the results obtained in multipole theory and with the dependence on the wave vector $k_\imath$.
4. Space inversion, time reversal and intrinsic symmetries of the fields and of the polarizability tensors have to be maintained, also making use of the $\delta_{\imath\jmath}$ and $\varepsilon_{\imath\jmath k}$ tensors and of the wave vector $k_\imath$.
5. The material constants have to be independent of the fields $\boldsymbol{E}$ and $\boldsymbol{B}$.
6. The expressions for the material constants have to be origin independent, as required for observables quantities.

Applying constraint 2 to the gauge and Faraday transformations, the response fields $\boldsymbol{D}$ and $\boldsymbol{H}$ still satisfy the linear constitutive relations, but with transformed material constants (according to requirement 1). The transformed material constants are defined as:

$$A_{\imath\jmath} = A^M_{\imath\jmath} - \frac{1}{\omega}\varepsilon_{\imath kl} k_k U^G_{l\jmath} + \frac{1}{\omega}\varepsilon_{\jmath kl} k_k Z^F_{\imath l} \tag{5.26}$$

$$T_{\imath\jmath} = T^M_{\imath\jmath} - \frac{1}{\omega}\varepsilon_{\imath kl} k_k X^G_{l\jmath} + Z^F_{\imath\jmath} \tag{5.27}$$

$$U_{\imath\jmath} = U^M_{\imath\jmath} + U^G_{\imath\jmath} + \frac{1}{\omega}\varepsilon_{\jmath kl} k_k Y^F_{\imath l} \tag{5.28}$$

$$X_{\imath\jmath} = X^M_{\imath\jmath} + X^G_{\imath\jmath} + Y^F_{\imath\jmath} \tag{5.29}$$

where the tensors $U^G_{\imath\jmath}$, $X^G_{\imath\jmath}$, $Y^F_{\imath\jmath}$ and $Z^F_{\imath\jmath}$ have to be determined. Here the superscripts M, F and G refer to the tensors given by multipole theory, gauge transformations and Faraday's transformations, respectively. Note that, according to the first constraint and to the constitutive relations defined in eqs. (5.13) and (5.14), the gauge transformations transform the constitutive tensor A^M_{ij} in U^M_{ij} and T^M_{ij} in X^M_{ij}, whereas the Faraday's transformations shift A^M_{ij} in T^M_{ij} and U^M_{ij} in X^M_{ij} and viceversa.

In order to completely define the transformed material constants, it is necessary derive the expressions for the tensors U^G_{ij}, X^G_{ij}, Y^F_{ij} and Z^F_{ij}. The idea is to write down the most general expressions for them, taking linear combinations of all the independent, second-rank tensors, that are constructed to be linear and homogeneous in the macroscopic polarizabilities of a particular multipole order. Since I would like to include contributions up to the electric octopole-magnetic quadrupole order, as done in all the previous discussion, a wide number of polarizability tensors may contribute to the transformed material constants: α_{ij}, α'_{ij}, G_{ij}, G'_{ij} etc., plus all the possible combinations with the additional building blocks δ_{ij}, ε_{ijk} and k_i. Taking into account space inversion, time reversal, intrinsic symmetries and order of the polarizability tensors, 77 possible independent contributions have to be considered for non-magnetic mediums, whereas there are 76 for magnetic mediums[5].

In light of this analysis, it is possible write the most general expressions of the transformed material constants as linear combinations of macroscopic polarizabilities, where field-independent numerical coefficients appear. As an example of this approach, I am going to discuss the expression of the inverse permeability X_{ij} for a non-magnetic medium, since my work is focused on second-order magnetic properties. X_{ij} has been defined in eq. (5.29), where X^G_{ij} and Y^F_{ij} are:

$$X^G_{ij} = \beta_1 \chi_{ij} + \beta_2 \varepsilon_{ikl} H'_{klj} + \cdots + \beta_{24} \delta_{ij} d_{klkl} \tag{5.30}$$

$$Y^F_{ij} = \gamma_1 \chi_{ij} + \gamma_2 \varepsilon_{ikl} H'_{klj} + \cdots + \gamma_{24} \delta_{ij} d_{klkl} \tag{5.31}$$

The tensors included in these two equations are all time even, all the numerical coefficients β_i and γ_i are therefore real. Exploiting the constraints 2, 4 and 6, an origin-independent expression of the inverse permeability is obtained:

$$\begin{aligned} X_{ij} \;=\; & -\chi_{ij} + \frac{1}{2}\omega\{\varepsilon_{ikl}(H'_{jkl} + L'_{jkl}) \\ & + \varepsilon_{jkl}(H'_{ikl} + L'_{ikl}) - \omega[\frac{1}{3}(b_{ijkk} + b_{jikk}) - \frac{1}{2}d_{ikjk}] \\ & - \delta_{ij}[\varepsilon_{klm}H'_{klm} - \omega(\frac{1}{3}b_{kkll} - \frac{1}{4}d_{klkl})]\} \end{aligned} \tag{5.32}$$

---

[5] Complete lists of all the possible contributions can be found in ref.[8]. Here I will just report the guide lines of this approach.

The calculus is rather cumbersome and it requires some algebra. I would like to point out that the derivation and the final expression here are similar to those discussed in section 3.4.2, where an origin-independent expression of the frequency-dependent second-order magnetic response has been obtained. I will discuss this fact in more detail later in this chapter.

Note that transformation theory creates an infinite number of response fields, which become unique and physically acceptable only when the origin-independence and the symmetry requirements are imposed.

In exactly the same way, it is possible to derive expressions for all the transformed material constants, for both non-magnetic and magnetic mediums. In the case of non-magnetic mediums, we have:

$$T_{\imath\jmath} = -\frac{1}{2\omega}\varepsilon_{\imath kl}k_k X_{l\jmath} \tag{5.33}$$

$$U_{\imath\jmath} = \frac{1}{2\omega}\varepsilon_{\imath kl}k_k X_{l\jmath} \tag{5.34}$$

$$\begin{aligned} A_{\imath\jmath} \quad = \quad & \frac{1}{2}k_k k_l\{\frac{2}{\omega^2}\varepsilon_{\imath km}\varepsilon_{\jmath ln}\chi_{mn} - \frac{1}{\omega}\varepsilon_{\imath km}(H'_{\jmath ml} - L'_{\jmath lm}) \\ & - \frac{1}{\omega}\varepsilon_{\jmath km}(H'_{\imath ml} - L'_{ilm}) - \frac{1}{3}(b_{\imath\jmath kl} + b_{\jmath\imath kl}) + \frac{1}{2}d_{\imath k\jmath l}\} \end{aligned} \tag{5.35}$$

whereas for magnetic mediums:

$$\begin{aligned} X_{\imath\jmath} \quad = \quad & -\imath\chi'_{\imath\jmath} + \frac{\imath}{2}\omega\{\varepsilon_{\imath kl}(H'_{\jmath kl} + L'_{\jmath kl}) \\ & - \varepsilon_{\jmath kl}(H'_{\imath kl} + L'_{\imath kl}) - \omega[\frac{1}{3}(b'_{\imath\jmath kk} - b'_{\jmath\imath kk}) - \frac{1}{2}d_{\imath k\jmath k}]\} \end{aligned} \tag{5.36}$$

$$T_{\imath\jmath} = -\frac{1}{2\omega}\varepsilon_{\imath kl}k_k X_{l\jmath} \tag{5.37}$$

$$U_{\imath\jmath} = \frac{1}{2\omega}\varepsilon_{\imath kl}k_k X_{l\jmath} \tag{5.38}$$

$$\begin{aligned} A_{\imath\jmath} \quad = \quad & \frac{1}{2}k_k k_l\{-\frac{2}{\omega^2}\varepsilon_{\imath km}\varepsilon_{\jmath ln}\chi'_{mn} + \frac{1}{\omega}\varepsilon_{\imath km}(H_{\jmath ml} - L_{\jmath lm}) \\ & - \frac{1}{\omega}\varepsilon_{\jmath km}(H_{\imath ml} - L_{\imath lm}) + \frac{1}{3}(b'_{\imath\jmath kl} - b'_{\jmath\imath kl}) - \frac{1}{2}d'_{\imath k\jmath l}\} \end{aligned} \tag{5.39}$$

It is possible to see how the transformed magnetoelectric tensors $T_{\imath\jmath}$ and $U_{\imath\jmath}$ can be expressed in term of the transformed inverse permeability, and they have the same expressions in both cases.

Once more, I would like to emphasize that these expressions are origin-independent, by construction, and therefore are suitable to describe observable quantities. They also satisfy the symmetries introduced in eq. (5.24) for non-dissipative mediums and they can be extended to dissipative mediums too, where obviously the quoted symmetries will not be valid anymore, but still the origin-independence will be preserved[1],[7]. Eqs. (5.33), (5.34), (5.37) and (5.38) trivially satisfy the Post constraint: $T_{\imath\imath} = U_{\imath\imath}$, this is the reason why it has not been necessary include it in the list of constraints used to derive the transformed material constants.

It is important to note that transformation theory has been applied to the electric octopole-magnetic quadrupole order, thus the expressions of the transformed material constants, eqs. (5.32)-(5.39), refer to this order. Complete definitions of the transformed polarizability densities have to take into account also the electric dipole and the electric quadrupole-magnetic dipole terms. The procedure to obtain these contributions is identical to the one discussed above, actually much more simple, given that less polarizability tensors have to be considered at lower orders.

Considering the contributions given by the vacuum, the dipole, the electric quadrupole-magnetic dipole and the electric octopole-magnetic quadrupole, the complete definitions of the transformed material constants for non-magnetic mediums become[7],[8]:

$$\begin{aligned} A_{\imath\jmath} &= \varepsilon_0\delta_{\imath\jmath} + \alpha_{\imath\jmath} + \frac{1}{2}k_k k_l\{\frac{2}{\omega^2}\varepsilon_{\imath km}\varepsilon_{\jmath ln}\chi_{mn} \\ &\quad - \frac{1}{\omega}\varepsilon_{\imath km}(H'_{\jmath ml} - L'_{\jmath lm}) - \frac{1}{\omega}\varepsilon_{\jmath km}(H'_{\imath ml} - L'_{\imath lm}) \\ &\quad - \frac{1}{3}(b_{\imath\jmath kl} + b_{\jmath\imath kl}) + \frac{1}{2}d_{\imath k\jmath l}\} \end{aligned} \tag{5.40}$$

$$T_{\imath\jmath} = -\imath(G'_{\imath\jmath} - \frac{1}{2}\omega\varepsilon_{\jmath kl}a_{kl\imath}) - \frac{1}{2\omega}\varepsilon_{\imath kl}k_k X_{l\jmath} \tag{5.41}$$

$$U_{\imath\jmath} = -\imath(G'_{\jmath\imath} - \frac{1}{2}\omega\varepsilon_{\imath kl}a_{kl\jmath}) + \frac{1}{2\omega}\varepsilon_{\imath kl}k_k X_{l\jmath} \tag{5.42}$$

$$\begin{aligned} X_{\imath\jmath} &= -\chi_{\imath\jmath} + \frac{1}{2}\omega\{\varepsilon_{\imath kl}(H'_{\jmath kl} + L'_{\jmath kl}) \\ &\quad + \varepsilon_{\jmath kl}(H'_{\imath kl} + L'_{\imath kl}) - \omega[\frac{1}{3}(b_{\imath\jmath kk} + b_{\jmath\imath kk}) - \frac{1}{2}d_{\imath k\jmath k}] \\ &\quad - \delta_{\imath\jmath}[\varepsilon_{klm}H'_{klm} - \omega(\frac{1}{3}b_{kkll} - \frac{1}{4}d_{klkl})]\} \end{aligned} \tag{5.43}$$

whereas for magnetic mediums:

$$
\begin{aligned}
A_{\imath\jmath} &= \varepsilon_0\delta_{\imath\jmath} + \alpha_{\imath\jmath} - \imath\alpha'_{\imath\jmath} + \frac{1}{3}(a'_{\imath\jmath k} + a'_{\jmath k\imath} + a'_{k\imath\jmath})k_k \\
&\quad + \frac{1}{2}k_k k_l\{-\frac{2}{\omega^2}\varepsilon_{\imath km}\varepsilon_{\jmath ln}\chi'_{mn} + \frac{1}{\omega}\varepsilon_{\imath km}(H_{\jmath ml} - L_{\jmath lm}) \\
&\quad - \frac{1}{\omega}\varepsilon_{\jmath km}(H_{\imath ml} - L_{\imath lm}) + \frac{1}{3}(b'_{\imath\jmath kl} - b'_{\jmath\imath kl}) - \frac{1}{2}d'_{\imath k\jmath l}\}
\end{aligned}
\tag{5.44}
$$

$$
\begin{aligned}
T_{\imath\jmath} &= -\imath(G'_{\imath\jmath} - \frac{1}{2}\omega\varepsilon_{\jmath kl}a_{kl\imath}) + G_{\imath\jmath} - \frac{1}{3}G_{ll}\delta_{\imath\jmath} \\
&\quad - \frac{1}{6}\omega\varepsilon_{\jmath kl}a'_{kl\imath} - \frac{1}{2\omega}\varepsilon_{\imath kl}k_k X_{l\jmath}
\end{aligned}
\tag{5.45}
$$

$$
\begin{aligned}
U_{\imath\jmath} &= -\imath(G'_{\jmath\imath} - \frac{1}{2}\omega\varepsilon_{\imath kl}a_{kl\jmath}) - G_{\jmath\imath} + \frac{1}{3}G_{ll}\delta_{\imath\jmath} \\
&\quad + \frac{1}{6}\omega\varepsilon_{\jmath kl}a'_{kl\imath} + \frac{1}{2\omega}\varepsilon_{\imath kl}k_k X_{l\jmath}
\end{aligned}
\tag{5.46}
$$

$$
\begin{aligned}
X_{\imath\jmath} &= \frac{1}{\mu_0}\delta_{\imath\jmath} - \imath\chi'_{\imath\jmath} + \frac{\imath}{2}\omega\{\varepsilon_{\imath kl}(H'_{\jmath kl} + L'_{\jmath kl}) \\
&\quad - \varepsilon_{\jmath kl}(H'_{\imath kl} + L'_{\imath kl}) - \omega[\frac{1}{3}(b'_{\imath\jmath kk} - b'_{\jmath\imath kk}) - \frac{1}{2}d_{\imath k\jmath k}]\}
\end{aligned}
\tag{5.47}
$$

Again, the transformed material constants are origin-independent and satisfies the intrinsic symmetries by construction.

5.5 Transformed multipole moments densities

In the previous sections I have introduced the constitutive relations, eqs. (5.13) and (5.14), that describe the relations between the response fields $\boldsymbol{D}$ and $\boldsymbol{H}$ and the external fields $\boldsymbol{E}$ and $\boldsymbol{B}$ through the material constants; I have defined the response fields in terms of multipole moment densities, up to the electric octopole-magnetic quadrupole order, using multipole theory, eqs. (5.7) and (5.8); and I have derived the transformed material constants for non-magnetic and magnetic mediums, eqs. (5.40)-(5.47). Considering these expressions of the material constants, and comparing the constitutive relations with the definitions of the response fields in terms of multipole moment densities, it is possible to define the transformed multipole moment densities up to the electric octopole-magnetic quadrupole order. Here, I will not report their explicit expressions, since they are cumbersome and not relevant in my work[6], however I would like to emphasize that all the coefficients of the fields $\boldsymbol{E}$ and $\boldsymbol{B}$ and their gradients that appear in the quoted expressions are origin-independent polarizability densities. This is not surprising, given that the material constants used in the derivation are linear combinations of polarizabilities, origin-independent by construction.

5.6 Comments

A macroscopic analysis of molecular properties using multipole theory do not solve the problem of the origin dependence of the observable quantities. Thus, it has been necessary look for origin-independent expressions of the material constants, in order to have physically acceptable results. A relevant problem is to understand why multipole theory, that it is definitely a good theory to treat molecular properties, do not lead to origin-independent expressions of physical quantities, in the microscopic as well as in the macroscopic case. As noted in Chapter 3 when discussing the magnetizability, it is important to recognize which quantities are actually observables or not, that is, what we are effectively considering when we are doing a measurement, and how to connect them with the results obtained in multipole theory.
Microscopic and macroscopic analysis of molecular properties, using multipole theory, present several differences in the approaches and in the way to solve the problem of origin dependence. In the next section I will discuss this point in detail, considering the expression of the inverse permeability obtained in the macroscopic case, and comparing it with the analysis of the second-order magnetic response, previously done in the microscopic case.

5.7 Inverse permeability

Let consider the expression for the inverse permeability for non-magnetic mediums given in eq. (5.43). This expression has been obtained using multipole theory up to the electric octopole-magnetic quadrupole order, and applying the gauge and Faraday's transformations to the constitutive relations, in order to get an origin-independent definition of this molecular property. In eq. (5.32) only the terms given by the electric octopole-magnetic quadrupole order has been considered in the expression of the inverse permeability, whereas in eq. (5.43) all the possible contributions to it are included, given by the lower orders in the multipole expansion. Comparing these two

---

[6] Explicit expressions can be found in Ref.[8].

equations, it is clear that the only difference between them is the term $\frac{1}{\mu_0}\delta_{\imath\jmath}$, namely the contribution of the vacuum. Thus, it is possible claim that, in order to get an origin-independent expression of the inverse permeability, it is necessary to consider contributions up to the electric octopole-magnetic quadrupole order. In fact, if the multipole expansion is truncated at the electric quadrupole-magnetic dipole order, even acting with gauge and Faraday's transformations, no additional polarizabilities enter in the definition of this property, therefore the expression of the inverse permeability is simply:

$$X_{\imath\jmath} = \frac{1}{\mu_0}\delta_{\imath\jmath} - \chi_{\imath\jmath} \tag{5.48}$$

which is origin dependent according with the previous analysis.
In the light of this observation, we can see the importance to consider higher contributions in the multipole expansion, in order to have origin-independent definitions of molecular properties. Actually, it would be reasonable to consider neglecting some of the high-order contributions, given that they could appear small in magnitude compared to the foremost terms, but we would end up with unphysical results.
Let now compare the microscopic and the macroscopic analysis of magnetic properties. Recalling the discussion of chapter 3 for the microscopic case, it has been showed that the magnetizability is an origin-dependent quantities when an external frequency-dependent magnetic field is applied. An origin-independent expression has been derived by Raab and the Lange, and it has been reported in eq. (3.91). A similar situation occurs in the macroscopic case, where the magnetic property defined by multipole theory is origin dependent, thus it has been necessary look for an origin-independent expression for the inverse permeability, exploiting the non-unicity of the response fields and applying gauge and Faraday's transformations. Here, I recall the origin-independent expressions of the quoted magnetic properties[7]:

$$\begin{aligned} \chi_{\imath\jmath}(\omega) \;=\; & \chi_{\imath\jmath}(0) - \frac{1}{2}\omega\{\varepsilon_{\imath kl}(H'_{\jmath kl} + L'_{\jmath kl}) + \\ & + \varepsilon_{\jmath kl}(H'_{\imath kl} + L'_{\imath kl}) - \omega[\frac{1}{3}(b_{\imath\jmath kk} + b_{\jmath\imath kk}) - \frac{1}{2}d_{\imath k\jmath k}] + \\ & - \delta_{\imath\jmath}[\varepsilon_{klm}H'_{klm} - \omega(\frac{1}{3}b_{kkll} - \frac{1}{4}d_{klkl})]\} \end{aligned} \tag{5.49}$$

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[7] In the macroscopic case, I have considered the expression for non-magnetic mediums.

$$\begin{aligned}(5.50)\qquad X_{\imath\jmath} \;=\;& -\chi_{\imath\jmath} + \frac{1}{2}\omega\{\varepsilon_{\imath kl}(H'_{\jmath kl} + L'_{\jmath kl}) + \\ & + \varepsilon_{\jmath kl}(H'_{\imath kl} + L'_{\imath kl}) - \omega[\frac{1}{3}(b_{\imath\jmath kk} + b_{\jmath\imath kk}) - \frac{1}{2}d_{\imath k\jmath k}] + \\ & - \delta_{\imath\jmath}[\varepsilon_{klm}H'_{klm} - \omega(\frac{1}{3}b_{kkll} - \frac{1}{4}d_{klkl})]\}\end{aligned}$$

It is immediately clear that, except for the minus sign in the latter equation[8], these expressions are identical. However, the polarizabilities in these equations are differently defined in the two cases, since in the former equation they have been derived using a microscopic approach, whereas in the latter a spatial average of the microscopic multipole moments has been performed, in order to have the corresponding macroscopic definitions. Anyway, working on the definition of magnetic properties provided by multipole theory, origin-independent expressions have been derived as linear combination of polarizabilities, and these polarizabilities appear exactly in the same linear combination, in both the microscopic and the macroscopic cases. Thus, it would be possible to claim that, in the presence of a frequency-dependent magnetic field, origin-independent second-order magnetic properties resulting from the response of the system to the external perturbation are defined by equations (5.49) and (5.50), in the microscopic and macroscopic cases, respectively.

I would like to further investigate the differences between the microscopic and the macroscopic analysis. I have already discussed in detail in section 3.5 the procedure used by Raab and de Lange to derive an origin-independent expression of the second-order magnetic response, pointing out the weak point of their work.

Let now focus the attention on the macroscopic case. Here, an origin-independent expression for the inverse permeability, and in general of all the material constants, has been derived starting from the macroscopic Maxwell equations, and exploiting the non-unique definition of the response fields. In particular, this freedom in the definition of $\boldsymbol{D}$ and $\boldsymbol{H}$ suggested to introduce two sets of transformations, namely gauge and Faraday's transformations, that preserve the form of the macroscopic Maxwell equations, but modify the constitutive relations and the response fields themselves. These two sets of transformations are definitely suitable and consistent with the theory of electromagnetism, and no particular hypothesis have been done, except considering a complex harmonic form of the fields. In order to obtain origin-independent expressions of the material constants, a transformation theory established on

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[8] The minus sign occur because, in the macroscopic case, the "inverse" permeability has been considered.

the quoted gauge and Faraday's transformation has been applied. It has been necessary fix some constraints, vide supra, recalling that all the discussion is based on multipole theory. Analysing in detail this list of constraints, I would claim that all of them are mandatory and have to be satisfied by a general sets of transformations, in accordance with the theory of electromagnetism and the definition of an observable quantity. In fact, it is natural to ask to preserve the linearity of the constitutive relations, the order of the multipole expansions, and the symmetries of the fields and of the polarizability tensors. No further assumptions have been done, except of course to impose the origin independence of the material constants. Thus, the procedure followed in the macroscopic case appears to have a solid theoretical foundation that I would rather prefer to the one used in the microscopic case, where indeed suitable assumptions have been made, but the final expression for the second-order magnetic response has been derived just as a collection of polarizabilities, and not as the result of a consistent and exhaustive theoretical work.

Another aspect that prompt me to like better the macroscopic analysis, deal with its relativistic features[9]. In fact, a transformation theory has been applied, where the gauge and Faraday's transformations are based on the non-unique definition of the response fields in the Maxwell equations, which are purely relativistic and imply the linearity of the constitutive relations and the linear dependence of the fields and of the polarizabilities. Furthermore, the space inversion, time reversal and the intrinsic symmetries, imposed for non-dissipative mediums, are consistent within a relativistic framework. In particular, the symmetries of the material constants are achieved from a covariant, relativistic application of the classical field theory in macroscopic electromagnetism, using the Lagrangian formulation. However, it is important point out that the multipole expansions of the response fields $\boldsymbol{D}$ and $\boldsymbol{H}$ in terms of the fields $\boldsymbol{E}$ and $\boldsymbol{B}$ are not in general covariant.

In conclusion, the origin-independent expression for the magnetic response in the presence of an external frequency-dependent magnetic field obtained in the macroscopic approach, eq. (5.50), looks reliable and derived through a well-based relativistic theory. In contrast, the microscopic non-relativistic discussion leads to an equivalent result, but here the analysis is definitely less exhausting. Thus, I would in general consider equation (5.49) to be suitable and correct too, but a complete relativistic theory has still to be achieved, in order to justify this result.

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[9] I have already mentioned in the previous sections the reasons why I prefer to treat molecular properties in a relativistic framework.

Chapter 6

Remarks and conclusions

Here, I will briefly summarize the results obtained in the previous chapters, and I will discuss the possible future studies that could be performed on magnetic properties.

My work has been focused on a second-order magnetic property, namely magnetizability. Since, in the presence of a static magnetic field, the magnetizability is an observable quantity and its expression is origin independent, I would expect the same situation when a frequency-dependent magnetic field is applied. Instead, multipole theory provides an origin-dependent expression of the frequency-dependent magnetizability, I have thus tried to derive an origin-independent expression for this quantity. By definition, the expression of the magnetizability is constituted by two terms, diamagnetic and paramagnetic, where the latter is given by the magnetic dipole-magnetic dipole coupling; thus an origin-independent expression that include other multipole moment contributions has been rather named second-order magnetic response.

At first, I have analysed the magnetizability in the microscopic case and, in order to have a wide overview on the theoretical frame where its expression has been derived, electromagnetism, Lagrangian and Hamiltonian formalisms have been introduced. In particular, I have discussed the gauge issue in detail, since the choice of a specific gauge is fundamental in the analysis, and the problem of origin dependence of molecular properties could be considered equivalent to the problem of gauge origin in some specific cases. The multipole gauge provides an expansion of the vector and of the scalar potentials, and a Taylor expansion of the fields in terms of multipole moments, so it has been considered as the best choice of gauge, in order to study molecular properties and in particular the magnetizability.

The microscopic analysis has been done in the non-relativistic as well as in the relativistic framework, pointing out the differences between these approaches. The Hamiltonians are clearly different in the two cases, but this fact is particularly relevant when we are treating second-order magnetic response. In fact, the vector potential appears linear and quadratic in the non-relativistic Hamiltonian, but only linear in the relativistic Hamiltonian, thus in the former case the magnetizability shows two contributions, namely the diamagnetic and the paramagnetic, whereas in the latter only the paramagnetic contribution appears.

In the non-relativistic framework, I have showed the origin independence of the frequency-independent magnetizability, and I have discussed the work of Raab and de Lange, which have proposed an origin-independent expression of the second-order magnetic response, in the presence of a frequency-dependent magnetic field, as a collection of nine polarizabilities. Their work is based on a few suitable requirements that an origin-independent expression of the frequency-dependent magnetizability should fulfill, however it does not look to me that their derivation rely on a well-founded quantum theory. Thus, I have studied the magnetizability using another approach, namely working in the relativistic framework. I believe that this framework is much better than the non-relativistic one, given that the Maxwell equations play a central role in the discussion, and they are fully relativistic. Furthermore, the relativistic Hamiltonian, except for the fact that it is necessary to consider 4-component wave functions, is simpler, since it contains only a linear term in the vector potential. The relativistic expression for the second-order magnetic response has been introduced, showing that a shift of the origin of the coordinates produces the same displacement terms obtained in the non-relativistic case. I thought that a possible way to cancel these displacement terms was to include in the definition of second-order magnetic response the electric-quadrupole, since the magnetic dipole and the electric quadrupole appear at the same order in the multipole expansions of the potentials, and other observable quantities, such as optical rotation, have origin-independent expressions defined by a linear combination of the quoted contributions. Unfortunately, the same situation does not occur for the second-order magnetic response, and including in its expression the electric quadrupole moment does not solve the problem of origin dependence. Anyway, for the reasons mentioned above, I still believe that an origin-independent expression has to be derived within a relativistic framework. To this end, analysis of the multipole gauge and of the relativistic Hamiltonian seem to show the possibility to derive a gauge-independent interaction Hamiltonian, including terms of magnetic dipole-electric quadrupole order. Further discussions and work have to be done on this promising way, in order to derive an origin-independent expression of the second-order magnetic response.

Molecular properties have been discussed also in the macroscopic case. I have introduced the macroscopic Maxwell equations and the constitutive relations, where the latter define the relations between the response fields and the external fields through the material constants. As well as in the microscopic case, multipole theory lead to origin-dependent expression of the material constants, thus to unphysical results for observable quantities. A fundamental aspect in the macroscopic description is the non-unique definition of the response fields, which suggest the introduction of sets of transformations, namely gauge and Faraday's transformations. Fixing a few constraints that can be inferred from the analysis of the material constants, it has been possible to apply the quoted sets of transformations to the constitutive relations, and derive origin-independent expressions of the material constants. A fundamental feature of the gauge and Faraday's transformations is that they are based on the Maxwell equations, and they are therefore fully relativistic, thus the macroscopic analysis can be considered valid in a relativistic framework. The transformed material constants have been obtained considering contributions up to the electric octopole-magnetic quadrupole order, for non-magnetic and magnetic materials. Focusing on the magnetic response, namely the inverse permeability, it is possible to note that an origin-independent expression can be obtained only when the electric octopole-magnetic quadrupole contributions are considered, and that the resulting transformed expression is a linear combination of macroscopic polarizabilities, totally equivalent to the result obtained in the microscopic case. I consider satisfactory the origin-independent expression of the frequency-dependent magnetic response for non-magnetic and non-dissipative mediums, given in eq. (5.50), obtained in the macroscopic case.

Since in the microscopic case, an origin-independent expression of the second-order magnetic response shows an equivalent linear combination of polarizabilities, I would consider this expression reliable too. However, I do not think that the procedure followed to derive it is exhaustive, thus I believe it is still necessary discuss the microscopic case in detail, using a fully relativistic approach.

The microscopic expression for the second-order, frequency-dependent magnetic response, derived by Raab and de Lange, has been used to perform calculations by Krykunov and Autschbach[33]. In their paper, they have clearly separated the problem of gauge-origin dependence from the problem of origin dependence. The former can occur when both a static or a dynamic magnetic field are applied, and it is a consequence of the fact that the hypervirial relation, valid for complete basis set, has been used to show the origin independence of the static magnetizability. Since it is not possible use a complete basis set to perform calculations, this problem has been solved using gauge-including atomic orbitals (GIAO). The latter issue, widely discussed in my work, is a purely theoretical problem, and cannot be solved using GIAOs. Krykunov and Autschbach have calculated both the frequency-dependent magnetizability, that is an origin-dependent quantity, and the second-order magnetic response, using the expression of Raab and de Lange, showing that they converge to the same static limit. However, in the high frequency region, their behavior can be very different, since the expression of the magnetic response involves various different polarizabilities tensors.

Finally, I would like to mention the possible future studies that could be done on second-order magnetic properties.

In the macroscopic case, I believe that the expression given in eq. (5.50) is correct and it is based on a exhaustive theory. However, complex harmonic fields and the linearity of the constitutive relations have been used, thus an extension to more general cases, including non-linear contributions, could be achieved. Furthermore, considering harmonic plane waves, it is possible to derive a wave equation from the inhomogeneous Maxwell equations[34], and so express measurable quantities, as the refractive index, in terms of macroscopic polarizabilities, up to electric octopole-magnetic quadrupole order. In this way we could obtain experimental values of macroscopic polarizabilities, and compare them with calculations.

As I have already claimed, the microscopic expression for the second-order magnetic response needs a better theoretical explanation. I believe that it will be possible to recover the origin-independent expression for this property using a relativistic approach, and extend the analysis to more general external magnetic perturbations, as mentioned in the macroscopic case. I would not discard the possibility that an origin-independent expression of second-order magnetic response could have a different aspect, considering other forms of the external fields.

Note that several possible choices of gauge could be made, but I would still prefer the multipole gauge, considering the good results in general achieved for molecular properties using this choice of gauge.

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Appendix A

In this appendix I will show another possible way to demonstrate the origin-independence of the magnetizability in the static case. Let first consider the expression of the magnetizability given by the sum of eqs. (3.67) and (3.68). Using the definition of the angular momentum operator $\boldsymbol{l} = -\imath\hbar\boldsymbol{r}\wedge\nabla$, and operating a shift of the origin of the coordinate $\boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{d}$, the paramagnetic term can be rewritten as:

$$\begin{aligned} \boldsymbol{\chi}^{p'} &= -\frac{e^2}{4m^2} \ll (\boldsymbol{r}-\boldsymbol{d})\wedge\boldsymbol{p}; (\boldsymbol{r}-\boldsymbol{d})\wedge\boldsymbol{p} \gg_{\omega=0} = \\ &= \boldsymbol{\chi}^{p} + \frac{e^2}{4m^2}\{\ll \boldsymbol{l}; \boldsymbol{d}\wedge\boldsymbol{p} \gg_{\omega=0} + \ll \boldsymbol{d}\wedge\boldsymbol{p}; \boldsymbol{l} \gg_{\omega=0} + \\ &\quad - \ll \boldsymbol{d}\wedge\boldsymbol{p}; \boldsymbol{d}\wedge\boldsymbol{p} \gg_{\omega=0}\} \end{aligned} \tag{6.1}$$

Assuming an isotropic sample, it is possible to reduce the analysis of the magnetizability tensor by considering only its trace. Recalling the vector relations and the property of the trace, the term quadratic in the origin displacement takes the form:

$$\begin{aligned} & Tr \ll \boldsymbol{d}\wedge\boldsymbol{p}; \boldsymbol{d}\wedge\boldsymbol{p} \gg_{\omega=0} = \\ &= (\boldsymbol{G}\cdot\boldsymbol{G}) Tr \ll \boldsymbol{p}; \boldsymbol{p} \gg_{\omega=0} - \ll \boldsymbol{G}\cdot\boldsymbol{p}; \boldsymbol{G}\cdot\boldsymbol{p} \gg_{\omega=0} = \\ &= -Tr \ll (\boldsymbol{G}\cdot\boldsymbol{p})\boldsymbol{G} - (\boldsymbol{G}\cdot\boldsymbol{G})\boldsymbol{p}; \boldsymbol{p} \gg_{\omega=0} = \\ &= -Tr \ll \boldsymbol{G}\wedge(\boldsymbol{G}\wedge\boldsymbol{p}); \boldsymbol{p} \gg_{\omega=0} \end{aligned} \tag{6.2}$$

Considering the linear terms in the displacement, it is possible rewrite them as:

$$\ll \boldsymbol{l}; \boldsymbol{d}\wedge\boldsymbol{p} \gg_{\omega=0} = \ll \boldsymbol{d}\wedge\boldsymbol{p}; \boldsymbol{l} \gg_{\omega=0} = -m < 0 \mid \boldsymbol{G}\cdot\boldsymbol{r} - \boldsymbol{G}\boldsymbol{r} \mid 0 > \tag{6.3}$$

where the hypervirial relation and the Hermiticity of the linear terms have been used. It is important to remind that the hypervirial relation, introduced in eq. (3.76), is valid for an exact theory and in certain approximations, for a complete variational orbital basis set. Thus the paramagnetic part of the magnetizability, after the origin displacement, can be written as:

$$\begin{aligned} \boldsymbol{\chi}^{p\prime} &= \boldsymbol{\chi}^{p} - \frac{e^2}{4m^2}\{2m < 0 \mid \boldsymbol{G}\cdot\boldsymbol{r} - \boldsymbol{G}\boldsymbol{r} \mid 0 > + \\ &\quad + Tr \ll \boldsymbol{G}\wedge(\boldsymbol{G}\wedge\boldsymbol{p}); \boldsymbol{p} \gg_{\omega=0}\} \end{aligned} \tag{6.4}$$

Acting in a similar manner on the diamagnetic part, its expression becomes:

$$\begin{aligned} \boldsymbol{\chi}^{d\prime} &= \boldsymbol{\chi}^{d} + \frac{e^2}{4m^2}\{2m < 0 \mid \boldsymbol{G}\cdot\boldsymbol{r} - \boldsymbol{G}\boldsymbol{r} \mid 0 > + \\ &\quad + Tr \ll \boldsymbol{G}\wedge(\boldsymbol{G}\wedge\boldsymbol{p}); \boldsymbol{p} \gg_{\omega=0}\} \end{aligned} \tag{6.5}$$

It is clear that the additional terms, resulting from the shift of the origin of the coordinates, vanish. Therefore, in the presence of a time-independent external magnetic field, the expression of the magnetizability is origin-independent, assuming a complete variational basis set.