Chapter 1

Introduction to nonlinear optics

This first chapter provides an introduction to the optical nonlinear effects. The origin of the nonlinearities is described through two elementary models, allowing a first understanding of the nonlinear optics basics. The first model depicts the nonlinear interactions that occur in metals or in a plasma-gas. It is based on the dynamic behavior of a free gas of electrons subject to the Lorentz force. The second model describes the nonlinear interactions in a dielectric medium using a standard model based on the classical anharmonic oscillator. The chapter concludes on a review of the nonlinear effects.

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1 INTRODUCTION TO NONLINEAR OPTICS

1.1 Basics of nonlinear optics

In the following, a dielectric material is considered, which is composed of microscopic entities (atoms, molecules, ions...). The medium is then described as a collection of electric dipoles which, under the action of an external oscillating electric field $\mathbf{E}$, oscillate and radiate collectively a source term called the macroscopic polarization $\mathbf{P}$.

Nonlinear optical effects occur when the macroscopic polarization $\mathbf{P}$ magnitude is no longer proportional to the applied electric field amplitude $\mathbf{E}$. The polarization $\mathbf{P}$ is the source term that is included into Maxwell’s equations to describe the propagation of electromagnetic fields in a medium.

The relationship between $\mathbf{P}$ and $\mathbf{E}$ generally taking a complicated form, a first attempt consists in expressing the polarization in terms of a power series in the field strength:

$$\mathbf{P}(t) = \chi_1 \mathbf{E}(t) + \chi_2 \mathbf{E}(t)\mathbf{E}(t) + \chi_3 \mathbf{E}(t)\mathbf{E}(t)\mathbf{E}(t) + \cdots,$$

where the coefficients $\chi_i$ are taken constant as a first approximation. The power series expansion is valid as long as the amplitude of the incident field is much weaker than the atomic electric field strength.

The objective of the course is to describe more precisely the relationship between the incident electric field and the macroscopic polarization, including the determination of the coefficients $\chi_1$, $\chi_2$, $\chi_3$, which are respectively related to the linear regime, the second and the third order nonlinear regimes. The ability to generate a nonlinear polarization is responsible of numerous phenomena that will be illustrated in this course. One can cite the generation of a nonlinear polarization radiating at twice the frequency of an incident monochromatic wave. Such a phenomenon refers to the process of second-harmonic generation, which will be described in details in Chapter ??.

1.2 Physical origins of the optical nonlinearities

In order to introduce basic concepts of nonlinear optics, two simple models are presented that lead to a relationship between the applied field strength and the polarization in:

- metals or plasma-gas,
- dielectric media.

In the case of metals or plasma-gas, the model describes the motion of a free charge gas subject to the Lorentz force induced by an electromagnetic wave. The second model describes the motion of bound charges (electrons) under the action of an external field. A classical description of the electron motion gives rise to the determination of relationships for the induced dipole and for the macroscopic polarization.

In the linear regime, both models allow to retrieve expressions of the conductivity for metals and the susceptibility for dielectric medium. Beside the simplicity of those models, most of the nonlinear effects to be examined in more details in the following part of the course can be predicted.

1.2.1 Light-metals interaction

In the following, it is assumed that the electrical and optical properties of a metal can be represented in a similar manner by those of a free electron gas with a density $N$. The density of negative charges is compensated by a positive charge density, which is assumed to be fixed. In
1.2 Physical origins of the optical nonlinearities

In the case of a plasma-gas, the motion of the positive charges, which are heavier, should also be taken into account. The free electron gas is assumed dilute enough such as the charges interact with the electromagnetic field separately and independently of each others.

We consider the following electromagnetic wave propagating along the direction $z$:

\[
\begin{align*}
\mathbf{E} &= E_0 \cos(\omega t - kz)\mathbf{x} \\
\mathbf{B} &= B_0 \cos(\omega t - kz)\mathbf{y},
\end{align*}
\]

Assuming the case of a dilute gas, the relation between the magnetic and electric field amplitude is $B_0 = E_0/c$, with $c$ the speed of light in vacuum (dilute gas). In order to determine an expression for the induced polarization $\mathcal{P} = N\mathbf{p}$, with $\mathbf{p} = -e\mathbf{r}$ the induced dipole, one can solve the equation of motion for an electron, with a mass $m$, which is subject to the Lorentz force:

\[
m\frac{d^2 r}{dt^2} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}),
\]

where $\mathbf{v} = \frac{dr}{dt}$ defines the electron velocity. The previous equation neglects the friction forces. Substituting the field expressions (1.1), the equation of motion becomes:

\[
\begin{align*}
m\frac{d^2 x}{dt^2} &= -eE_0 \cos(\omega t - kz) + \frac{e}{c}E_0 \cos(\omega t - kz)\frac{dz}{dt} \\
m\frac{d^2 y}{dt^2} &= 0 \\
m\frac{d^2 z}{dt^2} &= -\frac{e}{c}E_0 \cos(\omega t - kz)\frac{dx}{dt}
\end{align*}
\]

Taking into account that the magnetic part of the Lorentz force can be neglected with respect to the electrical contribution, the equation of motion (1.3) is solved by means of a perturbative method, the sought solution being expressed as:

\[
r(t) = r^{(0)}(t) + r^{(1)}(t) + r^{(2)}(t) + \cdots,
\]

with $r^{(0)}$ the initial position of the electron, without any applied field, and $r^{(1)}$, $r^{(2)}$ the first and second order perturbative solutions resulting from the application of an external field. The first order solution is obtained by neglecting the magnetic contribution of the Lorentz force:

\[
r^{(1)}(t) = \frac{e}{m\omega^2}E_0 \cos(\omega t - kz)\mathbf{x} + O\mathbf{y} + O\mathbf{z}.
\]

The first order solution exhibits a linear relation between the motion of the electron and the electric field strength, along the direction of the electric field polarization state $\mathbf{x}$. The first order solution is then substituted in the right hand side of (1.3), enabling the derivation of the second order solution:

\[
r^{(2)}(t) = 0\mathbf{x} + 0\mathbf{y} - \frac{e^2}{8m^2c^2\omega^3}E_0^2 \sin(2(\omega t - kz))\mathbf{z}.
\]

This procedure can be reiterated to calculate the third order solution for the position of the electron.

Following the motion of the charges, a current density $\mathbf{j} = -Ne\frac{dr}{dt}$ and a polarization $\mathcal{P} = -Ner$ are generated within the free electron gas. The expression for the polarization will take the following form:

\[
\mathcal{P} = \mathcal{P}^{(1)}(t) + \mathcal{P}^{(2)}(t) + \mathcal{P}^{(3)}(t) + \cdots.
\]
The first order polarization term \( \mathbf{P}^{(1)}(t) \) is proportional to the strength of the applied field and corresponds to the linear polarization. Whereas, the second order polarization \( \mathbf{P}^{(2)}(t) \), related to \( (1.5) \), vibrates at the frequency \( 2\omega \) with a direction of polarization aligned along \( z \). This direction being orthogonal to the polarization states of \( \mathbf{E} \) and \( \mathbf{B} \), the second order polarization can not radiate in the medium, except in the vicinity of an interface or defects.

Finally, the expression of the third order polarization \( \mathbf{P}^{(3)}(t) \) is:

\[
\mathbf{P}^{(3)}(t) = -\frac{N e^4}{8 m^2 c^2 \omega^3} E_0^3 \left[ \cos(\omega t - kz) + \frac{1}{9} \cos 3(\omega t - kz) \right] \mathbf{x}.
\]

It shows that the medium can radiate a source term at the frequencies \( 3\omega \), and \( \omega \). The latter, whose amplitude depends on the square of the field is responsible for a nonlinear self-action of light in the medium.

In conclusion, we have shown that the origin of nonlinearities in metals and plasma-gas comes from the magnetic contribution of the Lorentz force. The ratio between the strength of the first, second and third order polarizations is given by \( e E_0 / mc \omega \).

Note that this model does not account for interactions between the charges that could be described introducing additional terms in the equation of motion. It does not either account for variations of the charge density in the electron gas.

### 1.2.2 Classical anharmonic oscillator model

A linearly polarized plane wave at \( \omega \) is propagating through a dielectric material. It interacts with the atoms or the molecules that constitute the material and induces a polarization \( \mathbf{P}(z, t) \):

\[
\mathbf{P}(z, t) = N \mathbf{p}(z, t),
\]

(1.6)

where \( \mathbf{p}(z, t) \) is the induced microscopic dipole and \( N \) the density of atoms or molecules. According to a classical description of this interaction, depicted in Fig. 1.1, the dipole originates from the modification of the trajectories of the valence electrons induced by the time varying external field through the Coulomb force. The motion of the ion cores is neglected.

Subsequently, the field amplitude of the linearly polarized monochromatic plane wave, which propagates along the direction \((Oz)\) with a wavevector \(k\), is given by:

\[
\mathbf{E}(z, t) = \left[ A(\omega) e^{-i(\omega t - kz)} + A(-\omega) e^{+i(\omega t - kz)} \right] \mathbf{x},
\]

\[
= E(\omega)e^{-i\omega t} + E(-\omega)e^{+i\omega t},
\]

where vector \( \mathbf{x} \) indicates the direction of polarization of the wave. The electric field \( \mathbf{E}(z, t) \) is assumed to be a purely real quantity. In the following, the conjugate of the complex field amplitude \( E(\omega) \) will be denoted by:

\[
E(\omega)^* = E(-\omega)
\]

(1.7)

**Notation:**

- \( \mathbf{E}(z, t) \) is a purely real quantity,
- \( E(\omega)^* = E(-\omega) \) is the complex conjugate of the complex field amplitude \( E(\omega) \)
For the sake of simplicity, we are considering an entity (atoms or molecules) with a single valence electron, with a uniaxial $x$ motion induced by an external electric field linearly polarized along the $x$ direction. The expression of the induced dipole is:

$$p(z, t) = -e x(z, t) x,$$

where the quantity $-e$ is the charge of one electron and the function $x(z, t)$ represents the instantaneous position of the electron. Its position is given with respect to its equilibrium position (no applied field). In order to get an expression for the polarization $P(z, t)$ induced by a given external field $E(z, t)$, one can solve the following equation of motion for the electron:

$$\frac{d^2 x}{dt^2} + \alpha \frac{dx}{dt} + \omega_0^2 x + \beta x^2 + \gamma x^3 + \cdots = \frac{-e}{m} x : E(z, t).$$

(1.9)

Conversely to the case of classical harmonic oscillator, we have voluntarily introduced restoring force terms that nonlinearly depend on the coordinate $x(z, t)$. Actually, the expression $\omega_0^2 x + \beta x^2 + \gamma x^3 + \cdots$ corresponds to the Taylor expansion of the restoring force. The right hand side term of (1.9) describes the driven Coulomb force. Considering the case of a dilute material, the local field is assumed to be equal to the macroscopic external field $E(z, t)$.

In general, this equation does not have an analytical solution with a simple expression. However, taking into account that the harmonic term $\omega_0^2 x$ dominates the anharmonic ones, the equation can be solved by means of a perturbation method for which the general solution takes the form:

$$x = \lambda x^{(1)} + \lambda^2 x^{(2)} + \lambda^3 x^{(3)} + \ldots,$$

(1.10)

where $\lambda$ is a parameter set between 0 and 1. Using such a perturbative approach, one can derive the expressions for the linear and nonlinear polarizations.

**Linear polarization**

Firstly, the anharmonicity terms are neglected (not included) and the equation of motion becomes:

$$\frac{d^2 x}{dt^2} + \alpha \frac{dx}{dt} + \omega_0^2 x = \frac{-e}{m} \left[ A(\omega)e^{-i(\omega t - k z)} + A(-\omega)e^{+i(\omega t - k z)} \right] x : x.$$

(1.11)

One solution of the driven regime (steady-state solution) takes the following form:

$$x^{(1)}(z, t) = a(\omega)e^{-i(\omega t - k z)} + a(-\omega)e^{+i(\omega t - k z)}.$$

(1.12)

Substituting (1.12) in (1.11) gives:

$$a(\omega) = \frac{-eA(\omega)}{mD(\omega)},$$

with $D(\omega) = \omega_0^2 - \omega^2 - i\alpha\omega$. Following the form of the driven solution (1.12), the induced dipole is directly proportional to the applied electric field:

$$p^{(1)}(z, t) = \alpha^{(1)}(\omega)A(\omega)e^{-i(\omega t - k z)} x + CC,$$
with $\alpha^{(1)} = \frac{e^2}{m\tilde{D}(\omega)}$ the first order polarizability (or linear polarizability) of the entity. If we assume that all the dipoles are identical and aligned along the single direction $x$, and since the linear susceptibility is defined by the relation

$$ \mathcal{P}^{(1)}(z, t) = \varepsilon_0 \chi^{(1)}(\omega)E(\omega)e^{-i\omega t} + CC, $$

one can find an expression of the linear susceptibility of the material:

$$ \chi^{(1)}(\omega) = \frac{Ne^2}{\varepsilon_0 m (\omega_0^2 - \omega^2 - i\alpha \omega)}. $$

The susceptibility is a complex quantity. The real part of the susceptibility is related to the dispersion of the material (the refractive index), while its imaginary part is related to the absorption (or gain) coefficient. The figure 1.2 shows the typical behavior of these two parts around the resonance frequency $\omega_0$.

As a first conclusion, we can say that the harmonic oscillator model well described the behavior of the linear susceptibility: we were able to recover the well known shape of the dispersive and absorption behavior of a material near to a resonance.

**2nd order nonlinear polarization**

The quadratic anharmonic term of the restoring force is now introduced in the equation of motion of the oscillator:

$$ \frac{d^2x}{dt^2} + \alpha \frac{dx}{dt} + \omega_0^2 x + \beta x^2 = -\frac{e}{m} x \cdot \mathcal{E}(z, t). $$

(1.14)

Considering a weak applied electric field, the quadratic term of the restoring force will be kept much smaller than the linear term. Assuming that $\beta x^2 \ll \omega_0^2 x$, one seeks a solution of the form:

$$ x(z, t) = \lambda x^{(1)}(z, t) + \lambda^2 x^{(2)}(z, t) + \cdots, $$

(1.15)

where $\lambda$ represents the strength of the perturbation and can be arbitrarily set between 0 and 1. This solution is substituted in (1.14), and considering that $x^{(1)}$ is the solution of (1.11), we find that $x^{(2)}$ is solution of the equation:

$$ \frac{d^2x^{(2)}}{dt^2} + \alpha \frac{dx^{(2)}}{dt} + \omega_0^2 x^{(2)} = -\beta \left(x^{(1)}\right)^2. $$

(1.16)
This equation describes the motion of a harmonic oscillator with a driven force proportional to \((x^{(1)})^2\), which contains oscillating terms at the frequencies \(\pm 2\omega\) and 0. One can seek a steady-state solution of the form:

\[
x^{(2)}(z, t) = b(0) + b(2\omega)e^{-2i(\omega t-kz)} + b(-2\omega)e^{+2i(\omega t-kz)}.
\]

After substitution in (1.16) and identification between the terms oscillating at the same frequency, we find the expressions:

\[
\begin{align*}
    b(0) &= \frac{-2\beta e^2|A|^2(\omega)}{m^2D(0)\hat{D}(\omega)\hat{D}(-\omega)}, \\
    b(\pm 2\omega) &= \frac{-\beta e^2A^2(\pm\omega)}{m^2D(\pm 2\omega)\hat{D}(\pm\omega)},
\end{align*}
\]

where \(\hat{D}(\omega) = \omega_0^2 - \omega^2 - i\alpha\omega\).

The expression for the second order induced dipole, which is proportional to \(x^{(2)}(z, t)\), is then:

\[
P^{(2)}(z, t) = 2\alpha^{(2)}(\omega, -\omega)A(\omega)A(-\omega)x + \alpha^{(2)}(\omega, \omega)A(\omega)A(\omega)e^{-2i(\omega t-kz)}x + CC,
\]

with

\[
\alpha^{(2)}(\omega_1, \omega_2) = \frac{\beta e^3}{m^2D(\omega_1 + \omega_2)\hat{D}(\omega_1)\hat{D}(\omega_2)},
\]

the second order polarizability of the material. Finally, a second order polarization and a second order nonlinear susceptibility can be defined by:

\[
P^{(2)}(z, t) = 2\epsilon_0\chi^{(2)}(\omega, -\omega)A(\omega)A(-\omega)x + \epsilon_0\chi^{(2)}(\omega, \omega)A(\omega)A(\omega)e^{-2i(\omega t-kz)}x + CC,
\]

with

\[
\chi^{(2)}(\omega_1, \omega_2) = \frac{N\alpha^{(2)}(\omega_1, \omega_2)}{\epsilon_0}.
\]

The total macroscopic polarization induced inside the material is then given by the sum:

\[
\mathcal{P}(z, t) = \mathcal{P}^{(1)}(z, t) + \mathcal{P}^{(2)}(z, t) = P^{(2)}(0) + P^{(1)}(\omega)e^{-i\omega t} + P^{(2)}(2\omega)e^{-2i\omega t} + CC.
\]

with:

\[
P^{(2)}(0) = 2\epsilon_0\chi^{(2)}(\omega, -\omega)E(\omega)E(-\omega)x
\]

\[
P^{(2)}(2\omega) = \epsilon_0\chi^{(2)}(\omega, \omega)E(\omega)E(\omega)x
\]

The macroscopic polarization being generated inside the material contains terms oscillating at the frequencies \(\omega\) (linear response), \(\omega = 0\) and \(\pm 2\omega\).

The expression (1.18) shows that the polarization that is radiated inside the materials contains new frequency components. The term with a frequency component at \(\omega = 0\) corresponds to the creation of a static field inside the material. This process is referred to as optical rectification. A second component radiated at the frequency \(2\omega\) describes the second harmonic generation (SHG) nonlinear effect. As in the case of the optical rectification, the amplitude of the polarization is proportionnal to the square of the applied electric field amplitude, which is the signature of a nonlinear response.
This simple model enables a description of the nonlinear response of dipoles excited by an external oscillating electric field. The nonlinear response originates from the anharmonicity in the restoring force that is no longer proportional to the deformation of the electronic cloud surrounding the nucleus. As the linear susceptibility, the nonlinear interaction can be strengthened once the frequency of the interacted electric fields is close to a material resonance.

An other comment concerns the wavevector related to the polarization component at 2ω, which is equal to 2k(ω). In general, it will differ from the wavevector k(2ω) of the electric field at 2ω and freely propagating along the direction z. The value of the wavevector k(2ω) is set through the dispersion relation of the material. However, the phase matching condition, in this case k(2ω) = 2k(ω), must be fulfilled in order to efficiently generate a beam at the second harmonic. If not, the nonlinear polarization at 2ω is not radiated in phase with the electric field at 2ω and the second-harmonic beam can not generated.

3rd order nonlinear polarization

Following the second order perturbation, the next step is the case of a dipole governed by a restoring force that contains a cubic term \( \omega_0^2 x + \gamma x^3 \). For simplification, we have omitted the quadratic term in this expression. The equation of motion for such a dipole is then given by:

\[
\frac{d^2 x}{dt^2} + \alpha \frac{dx}{dt} + \omega_0^2 x + \gamma x^3 = -\frac{e}{m} x \cdot \mathbf{E}(z, t). \tag{1.19}
\]

Actually, a material with a collection of dipoles governed by such an equation of motion exhibits a center of symmetry. Indeed, equation (1.19) remains the same after the following substitution : \( x \rightarrow -x \) and \( E \rightarrow -E \). The medium supports a centro-symmetry.

As in the previous cases, we seek a solution of (1.19) with the form given by (1.10). After substitution, one can show that the second order steady state solution vanishes and the equation of motion is reduced to:

\[
\frac{d^2 x^{(3)}}{dt^2} + \alpha \frac{dx^{(3)}}{dt} + \omega_0^2 x^{(3)} = -\gamma \left( x^{(1)} \right)^3. \tag{1.20}
\]

The motion is then equivalent to that of a harmonic oscillator driven by an external force containing terms oscillating at \( \pm \omega \) and \( \pm 3\omega \). The derivation of the previous equation exhibits the following expression for the third-order induced dipole:

\[
P^{(3)}(z, t) = 3\alpha^{(3)}(\omega, -\omega, \omega)A(\omega)A(-\omega)A(\omega)e^{-i(\omega t - k z)} x + \alpha^{(3)}(\omega, \omega, \omega)A(\omega)A(\omega)A(\omega)e^{-3i(\omega t - k z)} x + CC,
\]

with

\[
\alpha^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{-\gamma e^4}{m^3 \mathcal{D}(\omega_1 + \omega_2 + \omega_3) \mathcal{D}(\omega_1) \mathcal{D}(\omega_2) \mathcal{D}(\omega_3)},
\]

the third order polarizability of the material. Assuming that the dipoles are all oriented along the direction \( x \), the expressions for the third order polarization and third order nonlinear susceptibility are:

\[
P^{(3)}(z, t) = 3\epsilon_0 \chi^{(3)}(\omega, -\omega, \omega)A(\omega)A(-\omega)A(\omega)e^{-i(\omega t - k z)} x + \epsilon_0 \chi^{(3)}(\omega, \omega, \omega)A(\omega)A(\omega)A(\omega)e^{-3i(\omega t - k z)} x + CC,
\]

with

\[
\chi^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{N\alpha^{(3)}(\omega_1, \omega_2, \omega_3)}{\epsilon_0}.
\]

The total macroscopic polarization generated inside the material is then given by the sum:

\[
P(z, t) = P^{(1)}(z, t) + P^{(3)}(z, t)
\]

\[
= P(\omega)e^{-i\omega t} + P(3\omega)e^{-3i\omega t} + CC.
\]
and contains terms oscillating at the frequencies $\omega$ (with both a linear and nonlinear contribution) and $\pm 3\omega$.

The polarization term vibrating at the frequency $\pm 3\omega$ is responsible for the 3rd harmonic generation (THG):

$$ P^{(3)}(3\omega) = \varepsilon_0 \chi^{(3)}(\omega, \omega, \omega) E(\omega) E(\omega) E(\omega) x $$

Like the second harmonic generation, this nonlinear effect requires to fulfill a phase matching condition, which is given by the relation: $3k(\omega) = k(3\omega)$.

For the term vibrating at $\omega$, it is interesting to notice that it will affect the linear properties of the material. Indeed, the complex amplitude of the macroscopic polarization at $\omega$ is:

$$ P^{(3)}(\omega) = 3\varepsilon_0 \chi^{(3)}(\omega, -\omega, \omega) E(\omega) E(-\omega) E(\omega) x $$

$$ P(\omega) = P^{(1)}(\omega) + P^{(3)}(\omega) $$

$$ = \varepsilon_0 \left[ \chi^{(1)}(\omega) + 3\chi^{(3)}(\omega, -\omega, \omega) E(\omega) E(-\omega) \right] E(\omega) x $$

$$ = \varepsilon_0 \chi_{eff}^{(1)}(\omega) E(\omega) x. $$

This relation shows that the nonlinear response of the dipole at $\omega$ will modify the linear susceptibility $\chi^{(1)}(\omega)$ of the material through the quantity $3\chi^{(3)}(\omega, -\omega, \omega) E(\omega) E(-\omega)$. This modification is directly proportional to the field intensity and affects both the real part, which is related to the refractive index, and the imaginary part, related to the absorption (or gain). The modification of the refractive index refers to the optical Kerr effect, while the modification of the absorption refers to the two-photon absorption effect.