
Nonlinear Optics

INTRODUCTION - THE ORIGIN OF THE SUCEPTIBILITY

1.1 Literature

- “*Nonlinear Optics*”, 3rd Ed. by Robert Boyd, Academic Press (2008)
- “*Introduction to Nonlinear Optics*” by Geoffrey New, Cambridge Univ. Press (2011)
- “*Nonlinear Optics*” by G.I. Stegeman and R.A. Stegeman, Wiley (2012)

1.2 Introduction

Nonlinear optics reflects that under the action of an optical beam, the polarization of the material may depend non-linearly on the amplitude of the incident field. The origin of this nonlinearity is microscopic and depends on the material itself (atoms / molecules / crystalline network...) and they full theoretical treatment should be done with a quantum mechanical approach. Of course, the order of magnitude of the nonlinear response will differ from one material to another, but in fact, the number of basic nonlinear effects is relatively limited. Description of these effects is based on Maxwell’s equations, where the polarization is expanded as function of optical power.

In which experimental context is nonlinear optics used, and why is this field so important to study ?

- generation of soliton in optical fibers for applications in telecommunications
- parametric down conversion to generate entangled photon for secure telecommunications
- high-resolution microscopy based on multi-photon excitation
- high-resolution spectroscopy
- generation of ultra-short pulses
- many others...

1.3 Notations

For this lecture I have used different references and the notations often varies from one book to another. I have tried to be consistent with the notations for the whole lectures. Obviously mistakes can always happen and I encourage the reader to follow this notes with attention. Here are the conventions that I will use:

1. SI units are used.
2. The electric field is written as a superposition of monochromatic waves by using a Fourier transform:

$$E(t) = \mathcal{F} \left[\tilde{E}(\omega) \right] (t) = \int \tilde{E}(\omega) e^{-i\omega t} \frac{d\omega}{2\pi} \quad (1.1)$$

where

$$\tilde{E}(\omega) = \mathcal{F}^{-1}[E(t)](\omega) = \int E(t)e^{i\omega t} dt \quad (1.2)$$

is a complex quantity. Since the electric field is a real quantity, its Fourier transform has to be symmetric and therefore $\tilde{E}(\omega)^* = \tilde{E}(-\omega)$, where the * indicates the complex conjugate. The knowledge of the field for the positive frequencies is enough to reconstruct the whole electric field. We can then introduce the complex electric field by

$$\mathcal{E}(\omega) = 2\Theta(\omega)\tilde{E}(\omega) \quad (1.3)$$

where the Heaviside function $\Theta(\omega)$ insure that we only consider the values corresponding to the positive frequencies. Inversaly the electric field can be written from the complex field by

$$\tilde{E}(\omega) = \frac{1}{2}[\mathcal{E}(\omega) + \mathcal{E}^*(-\omega)] \quad (1.4)$$

and using the inverse Fourier transform defined by eq. (1.2) we have the electric field given by

$$E(t) = \frac{1}{2}[\mathcal{E}(t) + \mathcal{E}^*(t)] = \text{Re}[\mathcal{E}(t)] \quad (1.5)$$

Note that by using this notation we can easily introduce the amplitude $|\mathcal{E}(t)|$ and the phase $\phi(t)$ of the temporal signal such that

$$\mathcal{E}(t) = |\mathcal{E}(t)| e^{i\phi(t)} \quad (1.6)$$

3. Similarly we can introduce the complex polarization \mathcal{P} in order to express the material polarisation P by

$$P = \frac{1}{2}(\mathcal{P} + \mathcal{P}^*) \quad (1.7)$$

1.4 Dielectric susceptibility

Starting from the Maxwell equations:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (1.8a)$$

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \quad (1.8b)$$

$$\nabla \cdot \mathbf{D} = \rho \quad (1.8c)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (1.8d)$$

associated with the equations for the material:

$$\mathbf{B} = \mu_0 \mathbf{H} + \mathbf{M} \quad (1.9a)$$

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} \quad (1.9b)$$

for a dielectric ($\rho = 0$) and a non-magnetic medium ($\mathbf{M} = 0$), using the algebraic equation $\nabla \times \nabla \times \mathbf{A} = \nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}$ applied to eq. (1.8a), we derive the equation for the propagation of the electric field:

$$\left[\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right] \mathbf{E} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 \mathbf{P}}{\partial t^2} \quad (1.10)$$

As we will see, the polarization depends directly on the electric field. Therefore, the field induces a polarization, which then modifies the electric field itself. According to eq. (1.10), the polarization acts indeed as a source term on the electric field \mathbf{E} .

1.4.1 Linear aspect. Bound electron model.

In this picture, the electron is bound to the nucleus and the motion of that electron¹ can simply be modelled by an harmonic oscillator, which is forced by the incident electric field $E(t)$. Note that in this model the force on the electron is simply given by $\mathbf{F} = -e\mathbf{E}$ where only \mathbf{E} is the electric field and $(-e)$ the elementary charge for the electron. The magnetic field would need to be included if the electrons were relativistic, which is not the case here.

$$\frac{\partial^2 r}{\partial t^2} + \gamma \frac{\partial r}{\partial t} + \omega_0^2 r = -\frac{\bar{e}}{m_e} E(t) \quad (1.11)$$

where r represents the distance between the nucleus and the electron, $-\bar{e}$ is the elementary charge of the electron, γ a damping coefficient, and ω_0 is the resonance frequency of the system. Assuming a monochromatic wave, we can use the complex notation for the electric field

$$E(t) = \frac{1}{2} \mathcal{E}_0 e^{-i\omega t} + c.c. \quad (1.12)$$

and insert it in in eq. (1.11). We should now seek an oscillating solution for r . We readily obtain

$$r(t) = -\frac{\bar{e}}{m_e} \frac{\mathcal{E}_0}{2} \frac{e^{-i\omega t}}{(\omega_0^2 - \omega^2) - i\gamma\omega} + c.c. = \frac{-\bar{e}E(t)}{m_e D(\omega)} \quad (1.13)$$

where we introduce $D(\omega) = \omega_0^2 - \omega^2 - i\gamma\omega$. In the vicinity of a resonance ($\omega \simeq \omega_0$) $\Rightarrow |\omega - \omega_0| \ll \omega_0$ and therefore

$$\begin{aligned} D(\omega) &= (\omega_0^2 - \omega^2) - i\gamma\omega = (\omega_0 + \omega)(\omega_0 - \omega) - i\gamma\omega \\ &\simeq 2\omega_0(\omega_0 - \omega) - i\gamma\omega_0 \\ D(\omega) &\simeq -2\omega_0 \left[\Delta + i\frac{\gamma}{2} \right] \end{aligned}$$

where $\Delta = \omega - \omega_0$ leading to

$$r(t) \simeq \frac{\bar{e} E(t)}{2m_e\omega_0 \left(\Delta + i\frac{\gamma}{2} \right)} \quad (1.15)$$

We can then deduce the macroscopic polarization $P(t) = N(-\bar{e})r(t) = \epsilon_0 \chi^{(1)} E(t)$, where ϵ_0 is the vacuum permittivity, and $\chi^{(1)}$ the *linear susceptibility* is given by:

$$\chi^{(1)} = \frac{-N\bar{e}^2}{2m_e\omega_0\epsilon_0} \left[\frac{\Delta - i\gamma/2}{\Delta^2 + \gamma^2/4} \right]$$

¹In this picture, the mass of the nucleus $m_n \gg m_e$, the mass of the electron. Therefore only the electronic displacement is considered for the calculation of the dipole.

from which we can extract the real and imaginary parts:

$$\operatorname{Re} [\chi^{(1)}] = \frac{-N\bar{e}^2}{2m_e\omega_0\epsilon_0} \frac{\Delta}{\Delta^2 + \gamma^2/4} \quad (1.16a)$$

$$\operatorname{Im} [\chi^{(1)}] = \frac{+N\bar{e}^2}{2m_e\omega_0\epsilon_0} \frac{\gamma/2}{\Delta^2 + \gamma^2/4} \quad (1.16b)$$

Obviously, there exist several electronic resonances across the electromagnetic spectrum, and they will all contribute to the final susceptibility. Each resonance ω_k has not only its own absorption bandwidth γ_k but also contributes differently to the overall susceptibility, with a weight f_k . This results in

$$\chi(\omega) = \frac{N\bar{e}^2}{m_e\epsilon_0} \sum_k \frac{f_k}{(\omega_k^2 - \omega^2) - i\gamma_k\omega} \quad (1.17)$$

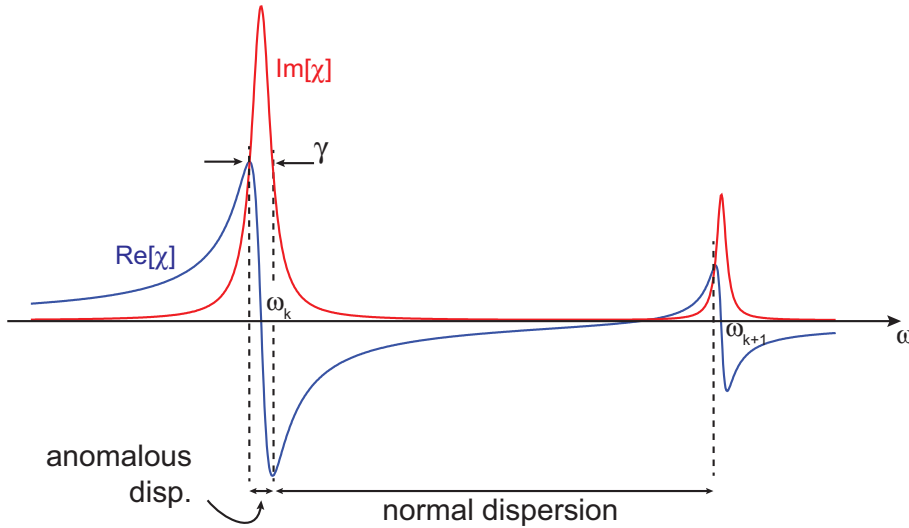


Figure 1.1: Overall susceptibility considering multiple resonances ω_k

Away from resonances, both *real* and *imaginary* part of the susceptibility increase. As it arrives in the vicinity of the resonance ω_i the real part reaches a maximum, then decreases rapidly and increase again. The phenomenon of rising permittivity (and therefore the refractive index $n = \sqrt{1 + \chi}$) with frequency characterizes the **normal dispersion**. The **anomalous dispersion** is when the permittivity and refractive index decrease with increasing frequency.

Far from any resonance, the damping coefficient ($\gamma_k\omega$) can be neglected, and we can express the refractive index as the so-called *Sellemeier equation*:

$$n = \sqrt{1 + \frac{N\bar{e}^2}{m_e\epsilon_0} \sum_k \frac{f_k}{(\omega_k^2 - \omega^2)}} \quad (1.18)$$

Sellmeier equations are usually given as a polynomial fit of the real part of the susceptibility, between two resonances. However we should keep in mind that *all the resonances* in the sum actually contribute to the real susceptibility χ even if we only look at a relatively narrow spectral region, *e.g.* the visible!

1.4.2 Order of magnitude

Let's consider the 1st laser ever demonstrated in 1960 by Théodore Maiman. It was a ruby laser, working at $\lambda = 694$ nm. Soon after its first demonstration, R.W. Hellwarth (1961) showed the possibility to generate strong pulses, in a so-called *Q-switch* regime. In this mode of operation, this laser can deliver 10^{18} photons in $\simeq 10$ ns.

$$\Rightarrow \text{Energy/pulse} : \frac{10^{18} \times hc}{\lambda} \simeq 0.3 \text{ Joule}$$

Such energy is not really much, but if we focus this laser down to $\simeq 100 \mu\text{m}^2$ then the density of energy, at the focus point is

$$\frac{0.3 \text{ Joule}}{10 \text{ ns} \times 100 \mu\text{m}^2} = 3 \times 10^{13} \text{ W} \cdot \text{cm}^{-2} = 30 \text{ TW} \cdot \text{cm}^{-2}$$

To estimate the magnitude of the electric field we need to use the relation

$$I = \frac{c\epsilon_0 n}{2} |E|^2 \quad \longrightarrow \quad E \simeq 10^{10} \text{ V/m}$$

Regarding an estimation of the intra-atomic field, we can simply use the Bohr radius², which leads to

$$E = \frac{13.6 \text{ V}}{0.53 \text{ \AA}} \simeq 10^{11} \text{ V/m}$$

As we see, the very first laser had already enough energy to provide an electric field comparable to the intra-atomic field. The analysis that we just did using the Lorentz formalism (bound-electron model) can then be legitimately questioned. Actually, under such conditions, the polarization will no longer be simply proportional to the incident electric field but will exhibit a nonlinear response

$$P = \epsilon_0 (\chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E}\mathbf{E} + \chi^{(3)} \mathbf{E}\mathbf{E}\mathbf{E} + \dots) \quad (1.19)$$

where $\chi^{(i)}$ is a $(i+1)$ th-rank tensor³. In a matrix form, this can be written as

$$\frac{P_i}{\epsilon_0} = \underbrace{\sum_j \chi_{ij}^{(1)} E_j}_{\substack{\text{linear part} \\ [absorption \& disp.] \\ 3 \times 3 = 9 \text{ elements}}} + \underbrace{\sum_{jk} \chi_{ijk}^{(2)} E_j E_k}_{\substack{\text{Pockels' term} \\ 3^3 = 27 \text{ elements}}} + \underbrace{\sum_{jkl} \chi_{ijkl}^{(3)} E_j E_k E_l}_{\substack{\text{Kerr effect} \\ 3^4 = 81 \text{ elements}}} + \dots \quad (1.20)$$

Note that in practice, the situation is much better than it looks. In the worst case, we will have 3 independent components, and most of the components of the tensor will be null.

²we remind that atomic Coulomb field which link the electron to the nucleus in the hydrogen atom is given by

$$E_{\text{atomic}} = \frac{\bar{e}}{4\pi\epsilon_0 r_B^2}$$

where the Bohr radius r_B is given by

$$r_B = \frac{4\pi\epsilon_0 \hbar}{m_e \bar{e}^2}$$

³We remind that 1st-rank tensor is simply a *vector* with 3 components. This means that a 2nd-rank tensor has $[3 \times 3]$ components, and so on.

1.5 Growth of interest – a few historical steps

Although **Kerr** and **Pockels**' effects were known prior to the first demonstration of the laser by Theodore Maiman in 1960, this is clearly this discovery which leads to the real use of nonlinear optics. If there were only three dates to remember, this would be

- 1960 \implies 1st demonstration of laser
- 1961 \implies demonstration second harmonic generation by Franken *et al.*
P.A. Franken *et al.*, Phys. Rev. Lett. **7**, 118-119 (1961)
- 1962 \implies seminal paper by Armstrong & co-workers on nonlinear optics
J.A. Armstrong *et al.* Phys. Rev. **127**, 1918 (1962)

One major aspect of nonlinear optics is that it allows converting one (or more) frequency into several others. Theory of OPO (optical parametric oscillator) was done in 1962, but the demonstration of such system only happened 3 years later. The lack of material was mainly the element that causes such a slow growth. Today, OPO and OPA (optical parametric amplifier) are very extensively used.

Nowadays, the improvement of nonlinear crystals, the semi-conductor hetero-structures, the photonic crystals and the quantum-confined material allow efficient uses of nonlinear optics. Another important factor was the discovery of *quasi phase matching* (QPM). Most devices relying on QPM require very thin layers of material and this technology is therefore challenging to realize. Efficiency for such highly-engineered material are extremely high.

As seen on eq. (1.48a), the polarization can involve either the Pockels' effect ($\chi^{(2)}$) or the Kerr effect ($\chi^{(3)}$):

Use of $\chi^{(2)}$	<ul style="list-style-type: none"> • OPO, OPA • Pockels' cells & electro-optic modulator • Second harmonic generation • characterization of ultra-short laser pulses
Use of $\chi^{(3)}$	<ul style="list-style-type: none"> • optical Kerr effect: <ul style="list-style-type: none"> - self-phase modulation, supercontinuum generation, temporal soliton - spatial self-focusing and spatial soliton • pulse compression, mode-locking • characterization of ultrashort laser pulses

We can also cite a series of coherent nonlinear optical processes such as *electromagnetically-induced transparency (EIT)*, *self-induced transparency (SIT)*, *slow light ...* etc. We will not be able to discuss all these effects during this whole lecture.

Finally, we cannot conclude this introduction without presenting the work from Rev. John Kerr (1824-1907) who discovered the so-called *Kerr effect*. John Kerr was a Scottish physicist who showed for the first time in 1875, that refractive index could be externally modified with an applied electric field. This modification, named the *Kerr electro-optic effect*, changes quadratically with the electric field. A few years later (1893), the German Friedrich Carl Alwin Pockels studied this problem, and showed that in specific cases (certain crystals), the application of an external field could lead to birefringence. By contrast with the Kerr effect, this effect varies linearly with the electric field. Moreover, this can only happens with crystals presenting a *lack of inversion symmetry* like lithium-niobate, KDP... etc.

1.6 Origin of the higher order of the susceptibility

In the Lorentz model of bound electron, the motion of the electron driven by the external electric field (*e.g.* a light beam) was written as

$$\ddot{\mathbf{r}} + \gamma\dot{\mathbf{r}} + \omega_0^2\mathbf{r} = -\frac{e}{m_e}\mathbf{E}(t) \quad (1.21)$$

where m is the mass of the electron, q its charge, and ω_0 the resonance of the system. Actually, we know that such an equation can be easily derived from the Newton 2nd law of motion:

$$\sum \mathbf{F} = m\mathbf{a} \quad (1.22)$$

where the forces \mathbf{F} acting on a mechanical system result in an acceleration \mathbf{a} .

1.6.1 Trivial case: the pendulum

In a very general frame, the harmonic oscillator can be written as

$$m\ddot{q} + kq = 0 \quad (1.23)$$

where q is the generalized coordinate. Multiplying by \dot{q} and integrating over dt leads simply to

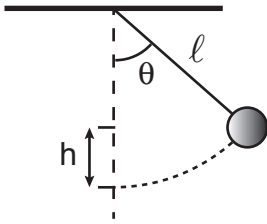
$$\frac{1}{2}m\dot{q}^2 + \frac{1}{2}kq^2 = \text{cste} = E_{\text{tot}} \quad (1.24)$$

Of course, this way of writing the equation of motion simply comes from the fact that any force can also be expressed with the help of a potential V as

$$\mathbf{F} = -\nabla V \quad (1.25)$$

In a very general form, we can then first write the conservation of total energy E_{tot} by

$$\frac{1}{2}m\dot{q}^2 + V(q) = E_{\text{tot}}. \quad (1.26)$$



For this system, potential energy and kinetic energy are simply given by

$$T = \frac{1}{2}m(\ell\dot{\theta})^2 \quad (1.27a)$$

$$V = mgh = mg\ell(1 - \cos\theta) \quad (1.27b)$$

Therefore the equation of the motion of the mass is

$$\begin{aligned} m\ell^2\ddot{\theta} + mg\ell\dot{\theta}\sin\theta &= 0 \\ \Rightarrow \ddot{\theta} + \frac{g}{\ell}\sin\theta &= 0 \end{aligned} \quad (1.28)$$

Of course, this example is well known, and this certainly one of the first nonlinear systems that you saw in your studied although you only looked at small angles when $\sin\theta \simeq \theta$ leading to a very simple potential and a linear system.

Already for slightly larger angle, this potential becomes more challenging to deal with:

$$E_p \underset{\theta \rightarrow 0}{\sim} mg\ell \left(\frac{\theta^2}{2} - \frac{\theta^4}{24} \right) \quad (1.29)$$

Note that the potential remains symmetric... In the current case, we are going to use a perturbative approach to solve the equation of motion when the potential does no longer exhibit a quadratic behaviour. Two cases must be studied:

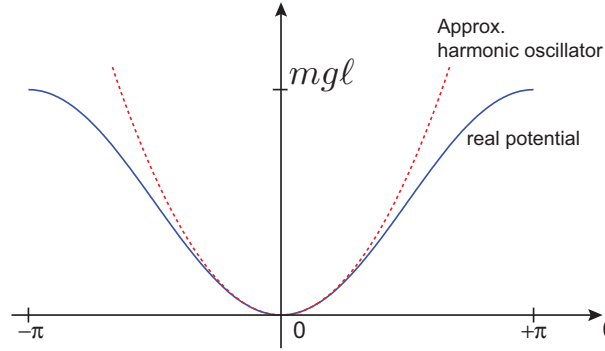


Figure 1.2: Real potential and harmonic approximation for the case of a pendulum.

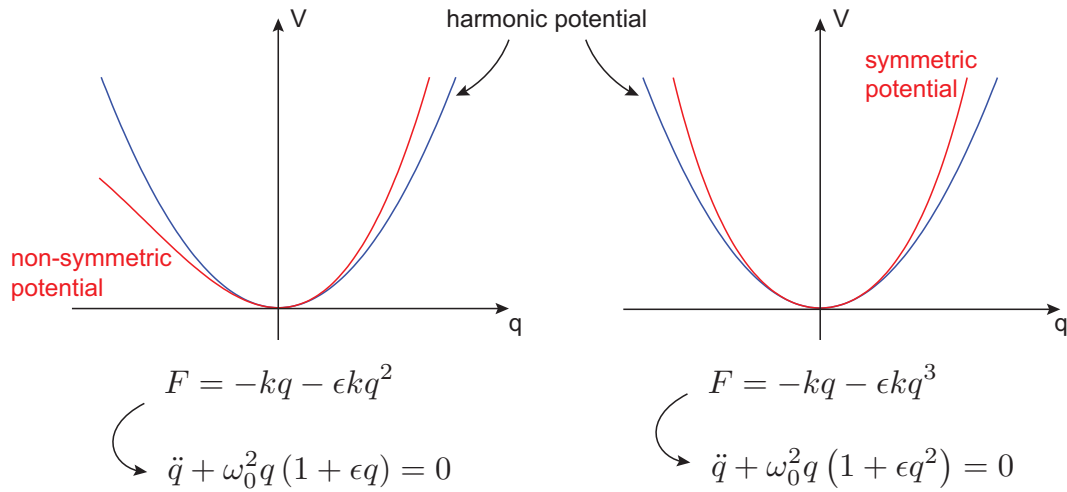


Figure 1.3: Different possibilities of nonlinear potentials

1.6.2 Asymmetric potential - far from electronic resonance

Here, we will suppose that the driving force is a single-eigenmode input. Moreover, we are only considering here that we work far from any electronic resonance, which means that the influence of any resonance is small. Therefore the damping can be described as $\epsilon\gamma\dot{q}$ where $\epsilon \ll 1$ and the driven frequency $\omega \neq \omega_0$. With such hypothesis, the electronic motion is

$$\ddot{q} + \epsilon\gamma\dot{q} + \omega_0^2 q(1 + \epsilon q) = -\frac{\bar{e}}{m_e} \frac{\mathcal{E}_0}{2} e^{-i\omega t} + c.c. = Ae^{-i\omega t} + c.c. \quad (1.30)$$

Assuming that the modification of the potential will affect the overall motion in a perturbative way, then

$$q(t) = q_0(t) + \epsilon q_1(t) \quad (1.31)$$

Inserting eq. (1.31) into eq. (1.30) gives

$$\begin{aligned} \ddot{q}_0 + \epsilon\ddot{q}_1 + \epsilon\gamma\dot{q}_0 + \omega_0^2 (q_0 + \epsilon q_1) (1 + \epsilon q_0) &= Ae^{-i\omega t} + c.c. \\ \Rightarrow \ddot{q}_0 + \epsilon\ddot{q}_1 + \epsilon\gamma\dot{q}_0 + \omega_0^2 q_0 + \epsilon\omega_0^2 q_0^2 + \omega_0^2 \epsilon q_1 &= Ae^{-i\omega t} + c.c. \end{aligned} \quad (1.32)$$

Looking at the different order in ϵ , we get:

$$\begin{aligned} [\epsilon^0] \quad & \rightarrow \quad \ddot{q}_0 + \omega_0^2 q_0 = A e^{-i\omega t} + c.c. \\ & \Rightarrow q_0 = \frac{A}{\omega_0^2 - \omega^2} (e^{-i\omega t} + c.c.) \end{aligned} \quad (1.33)$$

Since the macroscopic polarization is simply given by $P(t) = N(-e)q(t) = \epsilon_0 \chi^{(1)} E(t)$ then we can deduce the linear susceptibility that we already wrote:

$$\begin{aligned} P(t) = N(-\bar{e})q(t) &= N(-\bar{e}) \left(-\frac{\bar{e}}{m_e} \frac{\mathcal{E}_0}{2} \right) \frac{1}{\omega_0^2 - \omega^2} (e^{-i\omega t} + c.c.) = \epsilon_0 \chi^{(1)} \frac{\mathcal{E}_0}{2} (e^{-i\omega t} + c.c.) \\ &\Rightarrow \chi^{(1)}(\omega) = \chi^{(1)}(-\omega; \omega) = \frac{N\bar{e}^2}{m_e \epsilon_0} \frac{1}{(\omega_0^2 - \omega^2)} \end{aligned} \quad (1.34)$$

Remember that we are far from any resonance, and therefore, there is no contribution of the form $i\gamma\omega$ in the denominator. At the higher order in ϵ :

$$\begin{aligned} [\epsilon^1] \quad & \rightarrow \quad \ddot{q}_1 + \omega_0^2 q_1 = -\omega_0^2 q_0^2 - \gamma \dot{q}_0 \\ &= \frac{-\omega_0^2 A^2}{(\omega_0^2 - \omega^2)^2} [e^{-2i\omega t} + c.c. + 2] - \frac{\gamma \omega A}{(\omega_0^2 - \omega^2)} [-ie^{-i\omega t} + ie^{i\omega t}] \end{aligned} \quad (1.35)$$

As we can see, there are three different driving terms, oscillating at different frequencies: 0 (DC term), ω and 2ω ! For each forcing term, we can seek a solution as $q_1(t) = C e^{-ij\omega t} + c.c.$ with $j = 0, 1, 2$.

$$\begin{aligned} [0] : \quad & \ddot{q}_1 + \omega_0^2 q_1 = \frac{-2\omega_0^2 A^2}{(\omega_0^2 - \omega^2)^2} \\ & \rightarrow q_1(t) = \frac{-2A^2}{(\omega_0^2 - \omega^2)^2} \end{aligned} \quad (1.36)$$

$$\begin{aligned} [\omega] : \quad & \ddot{q}_1 + \omega_0^2 q_1 = \frac{-\gamma \omega A}{(\omega_0^2 - \omega^2)} [-ie^{-i\omega t} + c.c.] \\ & \rightarrow q_1(t) = \frac{+2\gamma \omega A}{(\omega_0^2 - \omega^2)^2} \sin(\omega t) \end{aligned} \quad (1.37)$$

$$\begin{aligned} [2\omega] : \quad & \ddot{q}_1 + \omega_0^2 q_1 = \frac{-\omega_0^2 A^2}{(\omega_0^2 - \omega^2)^2} [e^{-2i\omega t} + c.c.] \\ & \rightarrow q_1(t) = \frac{-\omega_0^2 A^2}{(\omega_0^2 - \omega^2)^2 (\omega_0^2 - 4\omega^2)} [e^{-2i\omega t} + c.c.] \end{aligned} \quad (1.38)$$

Finally the solution is

$$\begin{aligned} q(t) &= \frac{A}{\omega_0^2 - \omega^2} (e^{-i\omega t} + c.c.) \dots \\ &+ \underbrace{\frac{2\epsilon\gamma A}{(\omega_0^2 - \omega^2)} \sin(\omega t)}_{\substack{\text{contribution to absorption} \\ \text{very weak since } \epsilon \ll 1 \\ \text{and } \frac{\omega}{(\omega_0^2 - \omega^2)^2} \ll 1}} - \underbrace{\frac{2\epsilon A^2}{(\omega_0^2 - \omega^2)^2}}_{\text{continuous term: optical rectification}} - \underbrace{\frac{\epsilon \omega_0^2 A^2}{(\omega_0^2 - \omega^2)^2 (\omega_0^2 - 4\omega^2)} (e^{-2i\omega t} + c.c.)}_{\text{second harmonic generation}} \end{aligned} \quad (1.39)$$

As before, in order to get the susceptibility we use the expression for the polarization $P(t) = N(-\bar{e})q(t) = \epsilon_0 [\chi^{(1)}E(t) + \chi^{(2)}E^2(t)]$. Only considering the second terms, which are quadratic in E :

$$P^{(2)} = \epsilon_0 \chi^{(2)} E^2(t) = \epsilon_0 \chi^{(2)} \frac{\mathcal{E}_0^2}{4} (e^{-2i\omega t} + c.c. + 2) \quad (1.40)$$

$$P^{(2)}[0] = \epsilon \frac{\left(\frac{e^2}{m_e^2}\right) N e}{(\omega_0^2 - \omega^2)^2} \Rightarrow \chi^{(2)}(0; \omega, -\omega) = \epsilon \frac{N \left(\frac{e^3}{m_e^2}\right)}{2\epsilon_0 (\omega_0^2 - \omega^2)^2} \quad (1.41a)$$

$$P^{(2)}[2\omega] = \epsilon \frac{N e^3 \omega_0^2 \mathcal{E}_0^2}{4m_e^2 (\omega_0^2 - \omega^2)^2 (\omega_0^2 - 4\omega^2)} \Rightarrow \chi^{(2)}(2\omega; \omega, \omega) = \epsilon \frac{N \omega_0^2 \left(\frac{e^3}{m_e^2}\right)}{\epsilon_0 (\omega_0^2 - \omega^2)^2 (\omega_0^2 - 4\omega^2)} \quad (1.41b)$$

Note the typical notation for $\chi(\dots)$. The first 1st frequency in brackets is the result of the sum of the ones after the ; sign. In the more general case where two frequencies are used, we can do a similar calculation and find:

$$\chi^{(2)}(\omega_1 + \omega_2; \omega_1, \omega_2) = \epsilon \frac{N \left(\frac{e^3}{m_e^2}\right) \omega_0^2}{\epsilon_0 [\omega_0^2 - (\omega_1 + \omega_2)^2] (\omega_0^2 - \omega_1^2) (\omega_0^2 - \omega_2^2)} \quad (1.42a)$$

$$\chi^{(2)}(\omega_1 - \omega_2; \omega_1, -\omega_2) = \epsilon \frac{N \left(\frac{e^3}{m_e^2}\right) \omega_0^2}{\epsilon_0 [\omega_0^2 - (\omega_1 - \omega_2)^2] (\omega_0^2 - \omega_1^2) (\omega_0^2 - \omega_2^2)} \quad (1.42b)$$

At this stage it is legitimus to wonder whether the Taylor expansion is justified or not. The use of the perturbation theory will be fine as long as $P^{(i)} > 10P^{(i+1)}$. Let us look at the first term in the Taylor expansion of the polarization. Since $\chi^{(1)} \simeq n^2 - 1$ with $n = o(1)$ we can write

$$P = \epsilon_0 (\chi^{(1)}E + \chi^{(2)}EE + \dots) \implies \frac{P^{(1)}}{P^{(2)}} = \frac{\chi^{(1)}}{\chi^{(2)} E} \sim \frac{1}{\chi^{(2)} E_{\text{atom.}}} \simeq 10 \quad (1.43)$$

yielding $\chi^{(2)} \simeq 10^{-13} \text{m} \cdot \text{V}^{-1}$. Similarly the third order susceptibility will be $\chi^{(3)} \simeq 10^{-25} \text{m}^2 \cdot \text{V}^{-2}$. Note that these values are in the order of magnitude of the real values that you can find for various materials.

1.6.3 Symmetric potential

For the symmetric potential, the Lorentz model becomes:

$$\ddot{q} + \epsilon\gamma\dot{q} + \omega_0^2 q(1 + \epsilon q^2) = -\frac{e}{m_e} \frac{\mathcal{E}_0}{2} e^{-i\omega t} + c.c. = A e^{-i\omega t} + c.c. \quad (1.44)$$

As before, we are considering that we are far from any resonance ($\omega \neq \omega_0$) and that $\epsilon \ll 1$ so that we remain in the perturbative regime. As a consequence, we seek a solution as $q(t) = q_0(t) + \epsilon q_1(t)$. Inserting this ersatz in (1.44) gives

$$\begin{aligned}
 [\epsilon^0]: \quad \ddot{q}_1 + \omega_0^2 q_1 &= \frac{-2\omega_0^2 A^2}{(\omega_0^2 - \omega^2)^2} \\
 \rightarrow q_1(t) &= \frac{-2A^2}{(\omega_0^2 - \omega^2)^2} \quad (\text{this is the same as before!})
 \end{aligned}$$

$$\begin{aligned}
 [\epsilon^1]: \quad \ddot{q}_1 + \omega_0^2 q_1 &= -\gamma \dot{q}_0 - \omega_0^2 q_0^3 \\
 &= \frac{-\gamma \omega A}{(\omega_0^2 - \omega^2)} [-ie^{-i\omega t} + c.c.] - \frac{\omega_0^2 A^3}{(\omega_0^2 - \omega^2)^3} [e^{-3i\omega t} + 3e^{-i\omega t} + 3e^{i\omega t} + e^{3i\omega t}]
 \end{aligned}$$

And for the different frequencies of the driving term for the perturbative term:

$$\begin{aligned}
 [\omega]: \quad \ddot{q}_1 + \omega_0^2 q_1 &= \frac{-\gamma \omega A}{(\omega_0^2 - \omega^2)} [-ie^{-i\omega t} + c.c.] - \frac{3\omega_0^2 A^3}{(\omega_0^2 - \omega^2)^3} [e^{-i\omega t} + c.c.] \\
 \rightarrow q_1(t) &= -\frac{\gamma \omega A}{(\omega_0^2 - \omega^2)^2} [ie^{-i\omega t} + c.c.] - \frac{3\omega_0^2 A^3}{(\omega_0^2 - \omega^2)^4} [e^{-i\omega t} + c.c.] \\
 &= \frac{2\gamma \omega A}{(\omega_0^2 - \omega^2)^2} \sin \omega t - \frac{6\omega_0^2 A^3}{(\omega^2 - \omega^2)^4} \cos \omega t \tag{1.45}
 \end{aligned}$$

$$\begin{aligned}
 [3\omega]: \quad \ddot{q}_1 + \omega_0^2 q_1 &= \frac{-\omega^2 A^3}{(\omega_0^2 - \omega^2)^3} [e^{-3i\omega t} + c.c.] \\
 \rightarrow q_1(t) &= \frac{-\omega_0^2 A^3}{(\omega_0^2 - \omega^2)^3 (\omega_0^2 - 9\omega^2)} [e^{-3i\omega t} + c.c.] \tag{1.46}
 \end{aligned}$$

And finally the solution is:

$$\begin{aligned}
 q(t) &= \frac{A}{\omega_0^2 - \omega^2} (e^{-i\omega t} + c.c.) \dots \\
 &- \epsilon \frac{6\omega_0^2 A^3}{(\omega_0^2 - \omega^2)^4} \cos(\omega t) + \underbrace{\epsilon \frac{2\gamma \omega A}{(\omega_0^2 - \omega^2)^2} \sin \omega t}_{\text{weak contribution due to absorption}} - \underbrace{\epsilon \frac{\omega_0^2 A^3}{(\omega_0^2 - \omega^2)^3 (\omega_0^2 - 9\omega^2)} (e^{-3i\omega t} + c.c.)}_{\text{third harmonic generation}}
 \end{aligned} \tag{1.47}$$

As previously, we can write the polarization terms, and the susceptibilities:

$$P^{(3)}[\omega] = \epsilon \frac{N e^4 3 \omega_0^2 \mathcal{E}_0^3}{8 m_e^3 (\omega_0^2 - \omega^2)^4} \Rightarrow \chi^{(3)}(\omega; \omega, \omega, -\omega) = \epsilon \frac{3 N \omega_0^2 (e^4 / m_e^3)}{\epsilon_0 (\omega_0^2 - \omega^2)^4} \tag{1.48a}$$

$$P^{(2)}[3\omega] = \epsilon \frac{N e^4 \omega_0^2 \mathcal{E}_0^3}{8 m_e^3 (\omega_0^2 - \omega^2)^3 (\omega_0^2 - 9\omega^2)} \Rightarrow \chi^{(3)}(3\omega; \omega, \omega, \omega) = \epsilon \frac{N \omega_0^2 (e^4 / m_e^3)}{\epsilon_0 (\omega_0^2 - \omega^2)^3 (\omega_0^2 - 9\omega^2)} \tag{1.48b}$$

1.6.4 Origin of the asymmetry in the potential of $\chi^{(2)}$ materials

Since higher-order susceptibilities are only perturbative effect, their contribution should not totally modify the macroscopic polarization. In other words, a change $\mathbf{E} \rightarrow -\mathbf{E}$ should still leads to a change $\mathbf{P} \rightarrow -\mathbf{P}$ because the microscopic polarization is a measure of the field-induced deformation of the electronic cloud surrounding the nucleus, and the macroscopic polarization only a statistical average of the microscopic polarization over the material sample. As a result, $\chi^{(2)}$ materials must be structurally different from one direction to another.

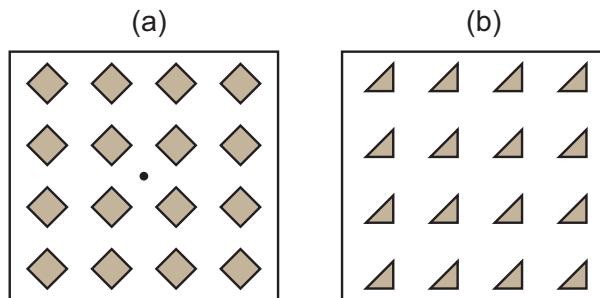


Figure 1.4: (a) centrosymmetric pattern and (b) non-centrosymmetric pattern [from. G. News, *Introduction to nonlinear optics*]

These materials have a *lack of inversion symmetry*, or a *lack of center of symmetry*, or are called *non-centrosymmetric*. Obviously glass material cannot present such properties because of the randomness of the arrangement of the molecules forming the glass. By contrast, crystal may present such specific unit cell. The table 1.1 presents the different classes of symmetry for the existing crystals, with their international notation (Hermann-Mauguin notation) as well as the number of independent number of independent elements for the tensor $\chi^{(n)}$. For crystals with lack of point symmetry, the number of independent elements for $\chi^{(2)}$ is obviously not relevant and indicated by a $-$ sign in the table.

As we will see, *biaxial* and *uniaxial* crystal are birefringent. We should point out here that the presence of birefringence does not imply that the crystal will also exhibit a lack of point symmetry.

class	system	International notation	Nbre of Indep. elements			Examples
			$\chi_{ij}^{(1)}$	$\chi_{ijk}^{(2)}$	$\chi_{ijkl}^{(3)}$	
Biaxial crystals	<i>Triclinic</i>	1	6*	18	81	Copper sulphate
		$\bar{1}$	6	-	81	
	<i>Monoclinic</i>	2	4*	8	41	LBO, KTP
		m	4	10	41	
		2/m	4	-	41	
	<i>Orthorhombic</i>	222	3*	3	21	LBO, KTP
		2mm	3	5	21	
2/m 2/m 2/m		3	-	21		
Uniaxial crystals	<i>Tetragonal</i>	$\bar{4}$	2	4	21	KDP, ADP Nickel sulphate
		4	2*	4	21	
		$\bar{4}2m$	2	2	11	
		422	2*	1	11	
		4/m	2	-	21	
	<i>Trigonal</i>	4/m 2/m 2/m	2	-	11	Sodium periodate
		3	2*	6	27	
		$\bar{3}$	2	-	27	
		32	2*	2	14	
		3m	2	4	14	
	<i>Hexagonal</i>	$\bar{3} 2/m = \bar{3}m$	2	-	14	Gallium selenide Lithium iodate β -quartz Cadmium selenide
		$\bar{6}=3/m$	2	2	19	
		$\bar{6}2m$	2	1	10	
		6	2*	4	19	
		622	2*	1	10	
		6/m	2	-	19	
		6mm	2	3	10	
		6/m 2/m 2/m	2	-	10	
		Optically isotropic crystals	<i>Cubic</i>	23	1*	
432	1*			-	4	
	3m = 2/m $\bar{3}$		1	-	7	Pyrite GaAs, zinc blende NaCl, diamond
	$\bar{4}3m$		1	1	4	
	4/m $\bar{3}$ 2/m		1	-	4	

Table 1.1: list of the 32 crystallographic point groups