Unit 1: Nonlinear optical response of materials

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Contents

The subject we will take up for the majority of this course is what we call *nonlinear optics*, which concerns itself with the interaction of high intensity electromagnetic radiation with materials.

I. THE FUNDAMENTAL IDEA: NONLINEAR RESPONSE TO LIGHT

Let us introduce nonlinear response by contrasting with the case of linear response. Suppose we apply an electric field to a material. All materials are polarizable to some extent: if an electric field is present inside them, then it will move charges around to induce polarization $\mathbf{P}$. In the linear electrodynamics of continuous media, we say that the polarization is linear in the electric field with some proportionality constant χ. The simplest linear relationship that one could write is

$$\mathbf{P}(\mathbf{r}, t) = \epsilon_0 \chi \mathbf{E}(\mathbf{r}, t). \tag{I.1}$$

This is an *instantaneous* and *local* relationship between the induced polarization and the electric field: the induced polarization at position $\mathbf{r}$ and time t depends on the electric field $\mathbf{E}$ at position $\mathbf{r}$ and time t. The electric field is the *total* electric field, which differs from the applied field insofar as the total field is the sum of the externally applied electric field and the electric field associated with the induced polarization.

The instantaneous, local relationship is not the most general linear relationship one could write. Indeed, if we think of the polarization as a linear functional of the electric field $\mathbf{P}[\mathbf{E}(\mathbf{r}, t)]$, then the most general linear relationship is one where the induced polarization $\mathbf{P}$ at $\mathbf{r}, t$ is a linear superposition of the electric field at all other positions and times [1].

$$\mathbf{P}(\mathbf{r}, t) = \epsilon_0 \int d\mathbf{r}_1 dt_1 \; \tilde{\chi}(\mathbf{r}, \mathbf{r}_1, t, t_1) \mathbf{E}(\mathbf{r}_1, t_1). \tag{I.2}$$

If we now ask: what is the most general functional $\mathbf{P}[\mathbf{E}]$, there is no reason why that relationship need be linear. We can however imagine that even if the relationship

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[1] You might object that the polarization cannot depend on spacetime points with spacelike separations, or even times *later* than the time in question. Both of these considerations work their way in as constraints on the linear susceptibility.

is *nonlinear*, for weak enough fields, we could approximate the relationship as linear. And indeed, that's the basic idea of nonlinear optics. The invention of the laser gave us access to focusable electromagnetic radiation of significant intensity to see the influence of the nonlinear terms in the polarization. In this class, we will develop the consequences of a nonlinear relationship between the polarization and electric field.

If the electromagnetic field is strong, but not *so* strong, we expect that we can represent the polarization in terms of a low-order Taylor expansion in powers of the electric field. We express this Taylor series as [2]

$$\mathbf{P}(\mathbf{r},t)=\sum_{n=1}^{\infty}\mathbf{P}^{(n)}(\mathbf{r},t), \tag{I.3}$$

where

$$P_i^{(n)}(\mathbf{r},t)=\epsilon_0\int\left(\prod_{i=1}^{n}d\mathbf{r}_i dt_i\right)\tilde{\chi}^{(n)}_{i,i_1,\cdots,i_n}(\mathbf{r},\mathbf{r}_1\cdots\mathbf{r}_n,t,t_1\cdots t_n)E_{i_1}(\mathbf{r}_1,t_1)\cdots E_{i_n}(\mathbf{r}_n,t_n). \tag{I.4}$$

In this expression, we have made use of repeated index notation: $T_{ij}a_ib_j=\sum\limits_{i,j}T_{ij}a_ib_j$. We will generally make use of repeated index notation. This expression while appearing complicated, is simply a dressed up multivariate Taylor expansion where the variables are $E_i(\mathbf{r},t)$: the electric field of a given component, at a given position, and a given time is treated as a variable [3]. The quantity $\tilde{\chi}^{(n)}_{i,i_1,\cdots,i_n}(\mathbf{r},\mathbf{r}_1\cdots\mathbf{r}_n,t,t_1\cdots t_n)$ is called the nth order nonlinear susceptibility.

Although it is relatively straightforward to understand how a relationship like this comes about, it is still extremely complicated, and we will need to simplify this. In this chapter we will develop general constraints on the form of the nonlinear susceptibility, which will arm us, in Chapter 2, to consider specific nonlinear interactions. We will illustrate these ideas by computing the nonlinear susceptibility for a specific microscopic model: a classical anharmonic oscillator. This microscopic model will also give us some indication of what electric field strengths are needed to

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[2] I omitted permament polarization, as in say a water molecule.

[3] Consider a scalar function $f(\mathbf{x})$ of n variables $x_1\cdots x_n$. Then the kth term in the multivariate Taylor expansion, expanded about $\mathbf{x}=0$ is (in repeated index notation) $\frac{1}{k!}\frac{\partial^k f}{\partial x_{i_1}\cdots\partial x_{i_k}}x_{i_1}\cdots x_{i_k}$. The derivative term is essentially the nonlinear susceptibility and we have expressed only the vector index sums in repeated index notation while treating the "sum" over continuous variables as integrals.

access nonlinearities. In this chapter, we will also see how the existence of these nonlinear responses allows for phenomena such as harmonic generation, sum-frequency generation, difference-frequency generation, and self-phase modulation.

II. CLASSICAL ANHARMONIC OSCILLATOR AS A MICROSCOPIC MODEL OF NONLINEAR RESPONSE

In this section, we will develop a simple concrete model of nonlinear optical response. This model will allow us to see: what is needed microscopically to get nonlinear response, what effects come from nonlinear response, why high-intensity is needed to access nonlinear effects, and many other general properties of nonlinear response tensors. This is a *very important section*: study it well, and you will have intuition about nonlinear optics *as a whole*.

A. Linear oscillator

Let us consider a rudimentary model of a polarizable material as a collection of independent and identical harmonic oscillators of density n, mass m, charge q, natural frequency ω_0, and damping constant γ. If the material is overall neutral and so the picture is that each element (atom) of the material is composed of one stationary charge of magnitude $-q$ (representing for example the nucleus which is much more massive than the electrons) and one movable charge of charge q (representing for example an electron). This model is called the *Lorentz oscillator*.

Each oscillator couples to the electric field $\mathbf{E}$. The equation of motion for the position $\mathbf{x}$ of each oscillator is

$$\ddot{\mathbf{x}} + \gamma\dot{\mathbf{x}} + \omega_0^2\mathbf{x} = \frac{q\mathbf{E}}{m}. \tag{II.1}$$

This equation is most readily solved in Fourier domain, and the solution can easily be seen to be

$$\mathbf{x}(t) = \int \frac{d\omega}{2\pi}\, e^{-i\omega t}\frac{q\mathbf{E}(\omega)/m}{D(\omega)}, \tag{II.2}$$

where $D(\omega) \equiv (\omega_0^2 - \omega^2) - i\gamma\omega$. Note that the frequency integration limits are $-\infty$ to ∞. The displacement of these charges constitutes a dipole. The polarization density is simply

$$\mathbf{P}(t) = nq\mathbf{x}(t) \leftrightarrow \mathbf{P}(\omega) = nq\mathbf{x}(\omega). \tag{II.3}$$

In frequency domain, we may then write that

$$\mathbf{P}(\omega) = \frac{nq^2}{mD(\omega)}\mathbf{E}(\omega), \tag{II.4}$$

which allows us to identify the linear susceptibility as

$$\chi^{(1)}(\omega) = \frac{nq^2}{m\epsilon_0 D(\omega)} = \frac{nq^2}{m\epsilon_0}\frac{1}{(\omega_0^2 - \omega^2) - i\gamma\omega}. \tag{II.5}$$

The permittivity is related to the susceptibility by $\epsilon = \epsilon_0(1 + \chi^{(1)})$ and the index of refraction by $n = \sqrt{\epsilon/\epsilon_0}$. I have neglected the tensorial nature of the permittivity since the response to all field directions is the same. Therefore as a tensor, we have $\chi^{(1)}_{ij} = \chi^{(1)}\delta_{ij}$. If the natural frequency and damping constants were *different* in different directions $\omega_{0,x}^2 \neq \omega_{0,y}^2 \neq \omega_{0,z}^2$ (where x, y, z refer to three orthogonal principal directions), then we get $\chi_{ii}(\omega) = \frac{nq^2}{m\epsilon_0 D_i(\omega)}$, where $D_i(\omega) = (\omega_{0,i}^2 - \omega^2) - i\gamma_i\omega$ (and $\chi_{ij} = 0$ if $i \neq j$).

Let us review the important limits of this Lorentz oscillator.

1. At low frequencies, $\omega \ll \gamma, \omega_0$ we have that the permittivity is *constant* and real, and given by $nq^2/m\epsilon_0$: this is the static permittivity. At frequencies $\omega_0 \gg \omega \gg \gamma$, one gets the same result. Thus, for frequencies much smaller than the resonance frequency of the system, the permittivity is approximately non-dispersive (frequency-independent) and real. At optical ($\omega_0 \sim 10^1 6$rad/s) frequencies and for densities typical in solids ($10^{29}m^{-3}$), one gets a susceptibility of order 1.

2. On resonance, the susceptibility becomes *purely imaginary* $\chi(\omega) = inq^2/(m\epsilon_0\gamma\omega_0)$ and large in magnitude (compared to one) when $\gamma \ll \omega_0$. The imaginary part of the susceptibility is related to the rate of absorption of energy by the oscillator, and so on resonance, the large imaginary part of the susceptibility signifies strong absorption.

3. At high frequencies, the susceptibility goes to zero: this is because for high frequencies, the oscillator cannot keep up with the drive. The oscillator can

only respond to the field over a timescale ω_0^{-1} and so over that timescale the electric field looks like it flips sign many times, averaging out to nearly no driving force. This behavior, that the permittivity goes to zero at high frequencies, is universal to all materials.

B. Cubic oscillator

The solution to the Lorentz oscillator is *exact*, and the polarization is linear in the electric field. To get contributions which are nonlinear in the electric field, the potential has to be *anharmonic* (in other words, it has to be a non-quadratic potential). In this section, we consider the example of a *cubic anharmonic oscillator* in one dimension. The relevant equation of motion becomes

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x + max^2 = qE(t)/m. \tag{II.6}$$

This equation is not exactly soluble. We will solve it *perturbatively*, assuming that the linear Lorentz oscillator behavior dominates (we will check for self-consistency after solving this equation). We pursue a perturbation theory in powers of the electric field.

$$x(t) = \sum_{k=1}^{\infty} x_k[E^k](t), \tag{II.7}$$

where $x_k[E^k]$ is a functional which has k powers of the electric field. The sum starts from $k = 1$ since no field implies no response if the system does not have permanent dipole moments. To find the x_k: one can plug in the series expansion and equate terms order-by-order. In the quadratic term in the equation of motion, the lowest power of the electric field is two, and does not contribute to the solution for x_1. Therefore

$$\ddot{x}_1 + \gamma\dot{x}_1 + \omega_0^2 x_1 = qE(t)/m. \tag{II.8}$$

The solution is simply the Lorentz oscillator solution:

$$x_1(t) = \int \frac{d\omega}{2\pi}\, e^{-i\omega t}\frac{qE(\omega)/m}{D(\omega)}. \tag{II.9}$$

The first correction to the Lorentz oscillator behavior satisfies $\ddot{x}_2 + \gamma\dot{x}_2 + \omega_0^2 x_2 + ax_1^2 = 0$ and thus:

$$\ddot{x}_2 + \gamma\dot{x}_2 + \omega_0^2 x_2 = \int \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi} e^{-i(\omega_1+\omega_2)t}\frac{-a(q/m)^2E(\omega_1)E(\omega_2)}{D(\omega_1)D(\omega_2)}. \tag{II.10}$$

This can be solved by Fourier transformation. Fourier transforming both sides of the equation yields

$$\left[(\omega_0^2 - \omega^2) - i\gamma\omega\right] x_2(\omega) = \int \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\, 2\pi\delta(\omega - (\omega_1 + \omega_2)) \times \frac{-a(q/m)^2 E(\omega_1)E(\omega_2)}{D(\omega_1)D(\omega_2)}, \tag{II.11}$$

with solution

$$x_2(\omega) = \int \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\, 2\pi\delta(\omega - \omega_\sigma) \times \frac{-a(q/m)^2 E(\omega_1)E(\omega_2)}{D(\omega_\sigma)D(\omega_1)D(\omega_2)}, \tag{II.12}$$

where we have defined $\omega_\sigma = \omega_1 + \omega_2$. The corresponding nonlinear polarization is $P^{(2)}(\omega) = nqx_2(\omega)$. As advertised we have a nonlinear relationship between the polarization and the field, which should define a $\chi^{(2)}$. We can define the second-order nonlinear susceptibility as follows:

$$P^{(2)}(\omega) = \epsilon_0 \int \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\, 2\pi\delta(\omega - \omega_\sigma)\chi^{(2)}(\omega_1, \omega_2))E(\omega_1)E(\omega_2), \tag{II.13}$$

where

$$\chi^{(2)}(\omega_1, \omega_2) = -\frac{anq^3}{m^2\epsilon_0} \times \frac{1}{D(\omega_\sigma)D(\omega_1)D(\omega_2)}. \tag{II.14}$$

This definition is introduced to be consistent with standard texts in nonlinear optics. As can be very clearly seen, a field that has Fourier components at frequencies ω_1 and ω_2 generates polarization with Fourier components as $\omega_1 \pm \omega_2$. Why minus? Because a real electric field always has its Fourier components come in $\pm\omega$ (a real field satisfies $E(\omega) = E(-\omega)^*$).

1. *Harmonic generation*

One such consequence of this frequency-combining is second harmonic generation. If we have a field component at frequency ω_1 then one term in the polarization expansion is $P(2\omega) \sim \chi^{(2)}(\omega, \omega)E(\omega)^2$. Recalling from Maxwell's equations that a time-oscillating polarization at frequency ω produces a time-varying electric field at the same frequency, we see that by illuminating a material with second-order nonlinearity with a field at frequency ω, we can generate a new electric field at frequency 2ω. This is called second-harmonic generation and is how nearly all green lasers work. They are based on the frequency-doubling of a relatively intense infrared laser (often based on Nd:YAG).

2. Sum-frequency and difference-frequency generation

Similarly, if we have a field with frequency components ω_1 and ω_2, we can generate a new field with frequency $\omega_1 + \omega_2$: second harmonic generation is a special case. This is called sum-frequency generation. Also interesting is that a field at frequency $\omega_1 - \omega_2$ can be generated. This is called difference-frequency generation, and is an important technique for generating terahertz radiation. Consider a short optical pulse with complex field $E_0 e^{-i\omega_0 t} e^{-t^2/2\tau^2}$. It's Fourier transform is proportional to $e^{-(\omega-\omega_0)^2\tau^2}$: two frequency components separated by $\Delta\omega$ can combine to give a field at frequency Δ. As can be seen from the Fourier domain field, Δ can be arbitrarily close to zero, and so a terahertz field can be generated.

3. Optical rectification and Pockels effect

One also notices immediately from the preceding discussion of difference-frequency generation that *zero* frequency radiation can be generated by a second-order nonlinear medium. This is called optical rectification. The inverse process also exists. Suppose we have a superposition of a DC field and an AC field at frequency ω. Then there is a polarization that can be created at ω which is proportional to $E_{\mathrm{DC}}E(\omega)$. This looks like a *linear* relationship between the AC field and the polarization, and indeed, we can say that the DC field is changing the linear susceptibility! This is the Pockels effect, and leads to the ability to shift the phase of an incident light field with DC voltages. By applying a slow AC voltage, it is also possible to modulate the phase and amplitude of a light wave in time!

We have already seen that the presence of an anharmonic potential leads to sum and difference frequency generation (including harmonic generation and rectification as special cases), as well as the modulation of the linear index of refraction. The generation of new frequencies, and the modification of the linear index of refraction with an external control field, are in a sense, the main effects of nonlinear optics.

C. Quartic oscillator

We now explore the consequences of a quartic term in the potential. One might argue that the quartic term will provide sub-leading corrections to the cubic term. But the cubic term doesn't exist in a wide class of *centrosymmetric* materials. If the material looks the same upon inversion: $\mathbf{x} \to -\mathbf{x}$, then we expect that reversing the sign of an applied electric field would reverse the sign of the polarization. Even-order terms in the polarization expansion are incompatible with this requirement, thus forcing that all even-order nonlinear susceptibilities must vanish. Thus, in a centrosymmetric material, the lowest-order nonlinear polarization is the cubic term.

Let us consider a centrosymmetric quartic oscillator. The resulting tensor properties of the third-order nonlinear susceptibility depend on the exact symmetries of the potential. We will consider an oversimplified model and consider an *isotropic* potential of the form $V(\mathbf{x}) = \frac{1}{4}mb(\mathbf{r}\cdot\mathbf{r})^2$. The resulting equation of motion is

$$\ddot{\mathbf{x}} + \gamma\dot{\mathbf{x}} + \omega_0^2\mathbf{x} + b(\mathbf{x}\cdot\mathbf{x})\mathbf{x} = q\mathbf{E}(t)/m. \tag{II.15}$$

Pursuing a perturbation series in powers of the field, it is clear that the part of the field at linear order in the field is simply the Lorentz oscillator solution:

$$\mathbf{x}(t) = \int \frac{d\omega}{2\pi}\, e^{-i\omega t}\frac{q\mathbf{E}(\omega)/m}{D(\omega)}. \tag{II.16}$$

There is no term at quadratic order in the fields: the lowest order term that the cubic force term can generate is cubic in the electric field. The third-order response follows immediately as

$$\mathbf{x}_3(t) = \frac{-bq^3}{m^3}\int \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi} e^{-i\omega_\sigma t}\frac{(\mathbf{E}(\omega_1)\cdot\mathbf{E}(\omega_2))\,\mathbf{E}(\omega_3)}{D(\omega_\sigma)D(\omega_1)D(\omega_2)D(\omega_3)}, \tag{II.17}$$

with $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$. The resulting nonlinear polarization is then given by

$$\mathbf{P}^{(3)}(\omega) = \frac{-nbq^4}{m^3}\int \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi} 2\pi\delta(\omega-\omega_\sigma)\frac{(\mathbf{E}(\omega_1)\cdot\mathbf{E}(\omega_2))\,\mathbf{E}(\omega_3)}{D(\omega_\sigma)D(\omega_1)D(\omega_2)D(\omega_3)} \tag{II.18}$$

In component notation, this is

$$P_i^{(3)}(\omega) = \frac{-nbq^4}{m^3}\int \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi} 2\pi\delta(\omega-\omega_\sigma)\frac{(E_j(\omega_1)E_j(\omega_2))\,E_i(\omega_3)}{D(\omega_\sigma)D(\omega_1)D(\omega_2)D(\omega_3)}. \tag{II.19}$$

The corresponding third-order susceptibility follows as

$$\chi^{(3)}_{ijkl} = -\frac{nq^4}{m^3\epsilon_0}\frac{1}{D(\omega_\sigma)D(\omega_1)D(\omega_2)D(\omega_3)}\delta_{jk}\delta_{il} \tag{II.20}$$

In the expression for $P_i^{(3)}(\omega)$, it is very clear that we could have written it as

$$P_i^{(3)}(\omega) = \frac{-nbq^4}{m^3}\int \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}2\pi\delta(\omega-\omega_\sigma)\frac{\left(E_j(\omega_1)E_j(\omega_3)\right)E_i(\omega_2)}{D(\omega_\sigma)D(\omega_1)D(\omega_2)D(\omega_3)}, \quad \text{(II.21)}$$

in which case we might have written $\chi^{(3)}_{ijkl} = -\frac{nq^4}{m^3\epsilon_0}\frac{1}{D(\omega_\sigma)D(\omega_1)D(\omega_2)D(\omega_3)}\delta_{jl}\delta_{ik}$, or

$$P_i^{(3)}(\omega) = \frac{-nbq^4}{m^3}\int \frac{d\omega_1}{2\pi}\frac{d\omega_2}{2\pi}\frac{d\omega_3}{2\pi}2\pi\delta(\omega-\omega_\sigma)\frac{\left(E_j(\omega_2)E_j(\omega_3)\right)E_i(\omega_1)}{D(\omega_\sigma)D(\omega_1)D(\omega_2)D(\omega_3)}, \quad \text{(II.22)}$$

in which we would have written $\chi^{(3)}_{ijkl} = -\frac{nq^4}{m^3\epsilon_0}\frac{1}{D(\omega_\sigma)D(\omega_1)D(\omega_2)D(\omega_3)}\delta_{kl}\delta_{ij}$. These are of course all the same expression and so we instead elect (for reasons to be made clearer later) to write the third-order susceptibility in a manifestly permutation-invariant way. Thus, we settle on the expression

$$\chi^{(3)}_{ijkl} = -\frac{nq^4}{3m^3\epsilon_0}\frac{\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}}{D(\omega_\sigma)D(\omega_1)D(\omega_2)D(\omega_3)}. \quad \text{(II.23)}$$

1. Frequency generation

Compared to the case of second-harmonic generation, we see now that we can generate fields at frequencies $\omega_1 \pm \omega_2 \pm \omega_3$. One consequence of this is third-harmonic generation. There is also sum and frequency difference generation, just now involving three frequencies.

2. Self-phase modulation

A unique effect to third-order nonlinearity is self-phase modulation. This is associated with $\omega_1 = \omega, \omega_2 = \omega, \omega_3 = -\omega$ and always occurs (recall that any AC field has its Fourier components come in $\pm\omega$ pairs due to the reality of the field). This corresponds to a polarization at the *same* frequency as the field and acts as if the linear susceptibility were intensity dependent.

3. Cross-phase modulation

If we take $\omega_1 = \omega', \omega_2 = \omega, \omega_3 = -\omega$ then we get a polarization at frequency ω'. This corresponds to a change in the index of refraction at frequency ω' controlled by the intensity of the field at frequency ω'.

D. Estimating the nonlinear coefficients

We have assumed that the nonlinear polarization terms are small compared to the linear polarizations. Let us now estimate the electric fields required to violate this assumption, and more broadly, get a sense of the scale of the nonlinear coefficients. Let's consider the second-order susceptibility.

$$\chi^{(2)}(\omega_1, \omega_2) \approx -a \frac{nq^3}{\epsilon_0 m^2 D(\omega_1+\omega_2) D(\omega_1) D(\omega_2)}. \tag{II.24}$$

It is instructive to compute

$$\left| \frac{\chi^{(2)}(\omega_1, \omega_2)}{\chi^{(1)}(\omega_1)\chi^{(1)}(\omega_2)\chi^{(1)}(\omega_1+\omega_2)} \right| = \frac{am\epsilon_0^2}{n^2 q^4}. \tag{II.25}$$

This is simply a frequency-independent constant, and that this ratio is constant is the statement of Miller's Rule: the second-order susceptibility scales as the cube of the linear susceptibility up to a material-dependent constant. In principle, if we know a then we could find the magnitude of $\chi^(2)$. It may be estimated in the following way. Physically, we expect the perturbation series for the polarization be valid if the electron bound to an atom is not pulled "too far" from the atom (at which point the system becomes an ionized plasma). Let us define "too far" as a distance a_0 where a_0 is the electronic length scale (e.g., the Bohr radius). At this length, the linear and nonlinear energies should be comparable. If we focus on the response to *low-frequency* fields, it is clear that the field needed to remove an electron is similar to the *internal DC field* E_{int} of the solid. This can be estimated through a a hydrogenic model as

$$E_{\text{int}} \sim \frac{q}{4\pi\epsilon_0 a_0^2} \sim 5 \times 10^{11} \text{V/m}. \tag{II.26}$$

This is also the electric field at which the second-order polarization should be comparable to the linear or first-order polarization, indicating immediately that

$$\chi^{(2)} \sim 1/E_{\text{int}} \sim 2 \text{ pm/V}, \tag{II.27}$$

which agrees well with the typical order of magnitude. A similar argument furnishes that

$$\chi^{(n)} \sim 1/E_{\text{int}}^{n-1} \tag{II.28}$$

Let us note that “low-frequency” means $\omega \ll \omega_0$. For many systems $\omega_0 \sim 10$ eV! And so the IR and optical frequencies we typically use in nonlinear optics are effectively “zero-frequency”. This is of course not always the case - so be careful. But note further that in the low frequency limit, the effect of the damping goes away and so these materials become transparent, which is very useful from the standpoint of nonlinear optics.

III. PROPERTIES OF THE NONLINEAR SUSCEPTIBILITY

In this section, we work out a few key properties of the nonlinear susceptibility.

A. Locality

The relationship we wrote, (I.4) looks different than what is typically written in that we have allowed for a generally *nonlocal* response: the polarization at $\mathbf{r}$ could depend on the field at different points $\mathbf{r}'$. That is typically negligible in nonlinear optics constants as it is only important when the electric field actually *varies* on a scale comparable to the scale of variation of $\tilde{\chi}(\mathbf{r}, \mathbf{r}')$ (I have only retained two arguments here for clarity). That scale is the atomic scale, and since optical fields have negligible variations on this scale, the $\mathbf{r}'$ dependence is always integrated over in a way that has no dependence on the electric fields (since they can be pulled out of the spatial integrals). This leaves us with a simpler, spatially local relation:

$$P_i^{(n)}(\mathbf{r}, t) = \epsilon_0 \int \left(\prod_{i=1}^{n} dt_i \right) \tilde{\chi}^{(n)}_{i,i_1,\cdots,i_n}(\mathbf{r}, t, t_1 \cdots t_n) E_{i_1}(\mathbf{r}, t_1) \cdots E_{i_n}(\mathbf{r}, t_n). \qquad \text{(III.1)}$$

Note that in writing this, I have not necessarily assumed that the nonlinear response is the same at every point in space: as might be the case if I had a composite material. In other words, I do not necessarily take *space-translation invariance to be a given.* In a uniform bulk material, the $\mathbf{r}$ dependence would go away.

B. Time-translation invariance

Suppose we subject the system to a pulsed electric field $E(\mathbf{r},t)$[4] that arrives in some material at time $t = 0$. That is going to initiate polarization dynamics $P(\mathbf{r},t)$. Now suppose I shift this electric field in time so that the pulse arrives in the material at a time $t = t_0$. In other words: $E(\mathbf{r},t) \to E(\mathbf{r},t-t_0)$. The statement of time-translation invariance is that the resulting polarization response is *also* shifted in time: $P(\mathbf{r},t) \to P(\mathbf{r},t-t_0)$. If we do not explicitly modify our material in time (or modify it quickly enough), time-translation invariance can be taken to hold.

Time-translation invariance is a powerful constraint. Suppose we shift our electric field by time t_0, then we can write the resulting polarization as [5]:

$$P_i^{(n)}(\mathbf{r},t) = \epsilon_0 \int \left(\prod_{i=1}^{n} dt_i\right) \tilde{\chi}^{(n)}_{i,i_1,\cdots,i_n}(\mathbf{r},t,t_1\cdots t_n) E_{i_1}(\mathbf{r},t_1-t_0)\cdots E_{i_n}(\mathbf{r},t_n-t_0). \tag{III.2}$$

However, this must be equal to the polarization induced by the *undelayed* fields up to a delay. In other words, the left-hand side must also be equal to:

$$\epsilon_0 \int \left(\prod_{i=1}^{n} dt_i\right) \tilde{\chi}^{(n)}_{i,i_1,\cdots,i_n}(\mathbf{r},t-t_0,t_1\cdots t_n) E_{i_1}(\mathbf{r},t_1)\cdots E_{i_n}(\mathbf{r},t_n). \tag{III.3}$$

Taking $t \to t - t_0$ in the above equation implies that

$$\tilde{\chi}^{(n)}(t,t_1\cdots,t_n) = \tilde{\chi}^{(n)}(t-t_0,t_1-t_0\cdots,t_n-t_0), \tag{III.4}$$

where I have followed our practice of omitting the trivial space and direction labels. The nonlinear susceptibility is fully time-translation invariant. Let's go back to our relation for the nonlinear polarization and express it as:

$$P_i^{(n)}(\mathbf{r},t) = \epsilon_0 \int \left(\prod_{i=1}^{n} dt_i\right) \tilde{\chi}^{(n)}_{i,i_1,\cdots,i_n}(\mathbf{r},0,t_1-t\cdots t_n-t) E_{i_1}(\mathbf{r},t_1)\cdots E_{i_n}(\mathbf{r},t_n). \tag{III.5}$$

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[4] In this text, I will generally omit degrees of freedom if the relation holds for all possible values of the omitted degrees of freedom. In otherwords, if the relationship is an element-wise relationship. For example here, I have omitted the vector indices because time-translation symmetry holds for each vector component. We'll refer to this practice as omission of trivial labels. We will not always do this, and so if you think a label is missing, ask if the relation holds for all values of that label!

[5] You may wonder below why, in keeping with the practice of omitting trivial labels, I did not omit $\mathbf{r}$. This dependence is too important to omit!

We may always perform this shift. We may then define a function of only n time arguments: $\tilde{\chi}^{(n)}_{i,i_1,\cdots,i_n}(0, t_1 - t \cdots t_n - t) \to \chi^{(n)}_{i,i_1,\cdots,i_n}(t - t_1, \cdots, t - t_n)$, and define the nonlinear polarization at nth order by

$$P_i^{(n)}(\mathbf{r}, t) = \epsilon_0 \int \left(\prod_{i=1}^{n} dt_i \right) \chi^{(n)}_{i,i_1,\cdots,i_n}(\mathbf{r}, t - t_1, \cdots, t - t_n) E_{i_1}(\mathbf{r}, t_1) \cdots E_{i_n}(\mathbf{r}, t_n). \tag{III.6}$$

We will henceforth *always* write the susceptibility in this way and so we drop the tilde that we have been carrying around.

C. Frequency-domain representation of the susceptibility

The multi-convolutional form of the nonlinear polarization in (III.6) suggests a simpler relationship in frequency-domain. Frequency-domain is of course very important in optics because we often use light sources which are relatively narrow-band: in other words, they have a reasonably well-defined center frequency (this is even true of 100 femtosecond pulses). We may express the electric field in Fourier domain via

$$\mathbf{E}(\mathbf{r}, t) = \int \frac{d\omega}{2\pi}\, e^{-i\omega t} \mathbf{E}(\mathbf{r}, \omega) \leftrightarrow \mathbf{E}(\mathbf{r}, \omega) = \int dt\, e^{i\omega t} \mathbf{E}(\mathbf{r}, t). \tag{III.7}$$

Plugging this into (III.6) yields

$$P_i^{(n)}(\mathbf{r}, t) = \epsilon_0 \int \left(\prod_{i=1}^{n} dt_i \frac{d\omega_i}{2\pi} e^{-i\omega_i t_i} \right) \chi^{(n)}_{i,i_1,\cdots,i_n}(\mathbf{r}, t - t_1, \cdots, t - t_n) E_{i_1}(\mathbf{r}, \omega_i) \cdots E_{i_n}(\mathbf{r}, \omega_n), \tag{III.8}$$

which may be written as

$$P_i^{(n)}(\mathbf{r}, t) = \epsilon_0 \int \left(\prod_{i=1}^{n} \frac{d\omega_i}{2\pi} \right) e^{-i\omega_\sigma t} \chi^{(n)}_{i,i_1,\cdots,i_n}(\mathbf{r}, \omega_1, \cdots, \omega_n) E_{i_1}(\mathbf{r}, \omega_i) \cdots E_{i_n}(\mathbf{r}, \omega_n), \tag{III.9}$$

where $\omega_\sigma = \sum\limits_{i=1}^{n} \omega_i$. In Fourier domain, the nonlinear polarization may be written as

$$P_i^{(n)}(\mathbf{r}, \omega) = \epsilon_0 \int \left(\prod_{i=1}^{n} \frac{d\omega_i}{2\pi} \right) 2\pi \delta(\omega - \omega_\sigma) \chi^{(n)}_{i,i_1,\cdots,i_n}(\mathbf{r}, \omega_1, \cdots, \omega_n) E_{i_1}(\mathbf{r}, \omega_i) \cdots E_{i_n}(\mathbf{r}, \omega_n). \tag{III.10}$$

The intuitive content of this equation is that an nth order nonlinear response converts n fields at respective frequencies $\omega_1 \cdots \omega_n$ to a polarization at frequency $\omega_\sigma = \omega_1 + \cdots + \omega_n$.

1. A brief note on notation

The notation we are using here is not quite in keeping with Boyd and many other texts on nonlinear optics. For one, Boyd for example write frequency sums as discrete sums. This, in the instructor's view, is a very continuous-wave oriented picture where we think of light as consisting of a discrete sum of monochromatic frequencies. Of course, the discrete sum notation is more general than that! If we assume that our fields and nonlinear susceptibilities vary negligibly over some small frequency increment $\Delta\omega$, then we may write the Fourier integral as a Riemann sum. For a true sum of monochromatic waves, such that the field $\mathbf{E}(\omega) = \sum_n \delta(\omega - \omega_n)\mathbf{E}_n$, one could reduce the frequency integrations to sums weighted by the nonlinear susceptibilities evaluated at definite frequencies (being careful about regularizing the equations when two or more frequencies are identical).

Another notational departure is in the susceptibility. Almost all authors choose to write $\chi^{(n)}(\omega_1, \cdots, \omega_n)$ as $\chi^{(n)}(\omega_\sigma, \omega_1, \cdots, \omega_n)$ where one additional frequency argument is added at the beginning of the list of frequency arguments. This frequency is always ω_σ. This argument is strictly speaking redundant but is a useful reminder as to what polarization is being generated! I will usually *not* write it unless I want to make explicit connection to canonical texts in nonlinear optics (e.g., Boyd).

D. Reality of the fields

The fact that the fields are real and the polarization is real requires that the time-domain susceptibility is real:

$$\chi^{(n)}(\tau_1 \cdots \tau_n) = (\chi^{(n)}(\tau_1 \cdots \tau_n))^*. \tag{III.11}$$

This immediately implies upon taking the Fourier transform of both sides that

$$\chi^{(n)}(-\omega_1 \cdots - \omega_n) = (\chi^{(n)}(\omega_1 \cdots \omega_n))^*. \tag{III.12}$$

E. Intrinsic permutation symmetry

In Eq. (III.10), it is clear that $\omega_1 \cdots \omega_n$ and $i_1 \cdots i_n$ are dummy variables that get summed over [6]. Suppose we define "super-indices" $\alpha_k = (i_k, \omega_k)$ and write the integral in Eq. (III.10) as a sum, leading to the form:

$$P_i^{(n)}(\omega) = \epsilon_0 \sum_{\alpha_1 \cdots \alpha_n} 2\pi\delta(\omega - \omega_\sigma)\chi^{(n)}_{i,\alpha_1 \cdots \alpha_n} E_{\alpha_1} \cdots E_{\alpha_n}. \tag{III.13}$$

For any given set of distinct indices, there are $\mathcal{N}_p$ distinct permutations of them which are all summed over. Denote the sum over permutations for a *fixed* set of indices, $\alpha_1 \cdots \alpha_n$ as $\sum\limits_{\mathrm{P}[\alpha_1 \cdots \alpha_n]}$. Then

$$\sum_{\mathrm{P}[\alpha_1 \cdots \alpha_n]} = E_{\alpha_1} \cdots E_{\alpha_n} \sum_{\mathrm{P}[\alpha_1 \cdots \alpha_n]} \chi^{(n)}_{i,P[\alpha_1 \cdots \alpha_n]}. \tag{III.14}$$

We see that the susceptibility for any set of indices, is summed over all permutations of those indices. The resulting sum over permutations is clearly permutation symmetric. As a result, we are free to *define* the nonlinear susceptibility as being permutation symmetric with respect to the superindices (we cannot permute only the frequency indices, or only the spatial indices). We note that this is strictly speaking a choice, but it is a *harmless* choice because even if we defined the susceptibility to not have this permutation symmetry with respect to the superindices, we would only ever see its fully permutation-symmetric part [7]. Therefore, we *define* the susceptibility tensor to have the property

$$\chi^{(n)}_{i,P[\alpha_1 \cdots \alpha_n]} = \chi^{(n)}_{i,\alpha_1 \cdots \alpha_n}. \tag{III.15}$$

This property is called *intrinsic* permutation symmetry.

F. Causality

We have been taking the time integrals to run from $-\infty$ to ∞ implicitly. Of course, the response cannot precede the applied field. That immediately implies

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[6] I will refer to discrete sums and integrals both as sums when appropriate and indices and continuous variables both as variables when appropriate.

[7] The fully permutation symmetrized part of the tensor is $(\mathcal{N}_p!)^{-1} \sum\limits_{\mathrm{P}[\alpha_1 \cdots \alpha_n]} \chi^{(n)}_{i,P[\alpha_1 \cdots \alpha_n]}$

that the susceptibilities have Heaviside theta functions $\theta(t-t_i)$ inside of them for all time arguments. Using the property that $\theta(t-t_i)^2 = \theta(t-t_i)$, we may write for example:

$$\chi^{(n)}(\mathbf{r}, t-t_1, \cdots, t-t_n) = \chi^{(n)}(\mathbf{r}, t-t_1, \cdots, t-t_n)\theta(t-t_i) \text{ for any } i. \tag{III.16}$$

We can in fact multiply by any number of Heaviside functions of any time argument, so in general one could write

$$\chi^{(n)}(\mathbf{r}, t-t_1, \cdots, t-t_n) = \chi^{(n)}(\mathbf{r}, t-t_1, \cdots, t-t_n)\prod_{i=1}^{n}\theta(t-t_i)^{k_i}, k_i \in \mathbb{N}. \tag{III.17}$$

1. *Kramers-Kronig relations*

This relation implies a constraint between the real and imaginary parts of the Fourier transform of the response tensor, called the Kramers-Kronig relation. The relation follows from considering the Fourier representation of the Heaviside function,

$$\theta(t) = -\lim_{\eta\to 0}\int \frac{d\omega}{2\pi i}\,\frac{e^{-i\omega t}}{\omega + i\eta}. \tag{III.18}$$

and plugging it into (III.16). Fourier transforming both sides of the equation yields

$$\chi^{(n)}(\omega_1, \cdots, \omega_n) = -\lim_{\eta\to 0}\int \frac{d\omega}{2\pi i}\frac{\chi^{(n)}(\{\omega \neq \omega_i\}, \omega_i - \omega)}{\omega + i\eta}. \tag{III.19}$$

Shifting variables leads to

$$\chi^{(n)}(\omega_1, \cdots, \omega_n) = -\lim_{\eta\to 0}\int \frac{d\omega}{2\pi i}\frac{\chi^{(n)}(\{\omega \neq \omega_i\}, \omega)}{\omega_i - \omega + i\eta}. \tag{III.20}$$

To proceed, we need to make use of the distributional identity known as the Plemelj (or Sohotsky-Plemelj formula):

$$\lim_{\eta\to 0}\frac{1}{x - i\eta} = \mathcal{P}\left[\frac{1}{x}\right] + i\pi\delta(x), \tag{III.21}$$

where $\mathcal{P}$ denotes Cauchy principal value [8]. Using this identity, one arrives at

$$\chi^{(n)}(\omega_1, \cdots, \omega_n) = \frac{1}{i\pi}\mathcal{P}\int d\omega\frac{\chi^{(n)}(\{\omega \neq \omega_i\}, \omega)}{\omega - \omega_i}, \tag{III.22}$$

---

[8] The Cauchy principal value is a distribution defined such that $\mathcal{P}\int dx\frac{f(x)}{x-a} = \lim_{\epsilon\to 0}\left[\int^{a-\epsilon} + \int_{a+\epsilon}\right] f(x)$. In other words we integrate “everywhere except a”.

which is the statement of the Kramers-Kronig relation.

The Kramers-Kronig relation is most commonly stated as a relationship between the real and imaginary parts of the function. For example, taking the real part of (III.22), we have

$$\text{Re } \chi^{(n)}(\omega_1, \cdots, \omega_n) = \frac{1}{\pi}\mathcal{P} \int d\omega \frac{\text{Im } \chi^{(n)}(\{\omega \neq \omega_i\}, \omega)}{\omega - \omega_i}, \tag{III.23}$$

and

$$\text{Im } \chi^{(n)}(\omega_1, \cdots, \omega_n) = -\frac{1}{\pi}\mathcal{P} \int d\omega \frac{\text{Re } \chi^{(n)}(\{\omega \neq \omega_i\}, \omega)}{\omega - \omega_i}, \tag{III.24}$$

2. Linear case

The by-far most useful application of Kramers-Kronig relations in optics is for *linear susceptibilities*. Although this is a course on nonlinear optics, this is a very important result and is often not covered in intermediate-level electrodynamics courses, so we discuss it here. In the linear case, we have

$$\text{Re } \chi^{(1)}(\omega) = \frac{1}{\pi}\mathcal{P} \int d\omega \frac{\text{Im } \chi^{(1)}(\omega')}{\omega' - \omega}, \tag{III.25}$$

and

$$\text{Im } \chi^{(1)}(\omega) = -\frac{1}{\pi}\mathcal{P} \int d\omega \frac{\text{Re } \chi^{(1)}(\omega')}{\omega' - \omega}. \tag{III.26}$$

The reality property for the linear susceptibility $\chi^{(1)}(\omega) = (\chi^{(1)}(-\omega))^*$ implies that the real part is even under frequency-domain reflection and the imaginary part is odd. We may use that to write the frequency integrals as ones with integration limits $0, \infty$ as

$$\text{Re } \chi^{(1)}(\omega) = \frac{2}{\pi}\mathcal{P} \int_0^\infty d\omega' \frac{\omega' \text{Im } \chi^{(1)}(\omega')}{\omega'^2 - \omega^2}. \tag{III.27}$$

For the imaginary part, we have

$$\text{Im } \chi^{(1)}(\omega) = -\frac{2\omega}{\pi}\mathcal{P} \int_0^\infty d\omega' \frac{\text{Re } \chi^{(1)}(\omega')}{\omega'^2 - \omega^2}. \tag{III.28}$$

A famous consequence of these relationships is that if the real part of the susceptibility (related to the index of refraction) is frequency-independent *everywhere* then the imaginary part of the susceptibility is zero identically. One may quickly check this from (III.27).

IV. DISPERSIONLESS NONLINEAR MEDIA

In general, the nonlinear susceptibility depends on all of its frequency arguments. For materials where the polarization approximately responds instantaneously to the field, the susceptibility is *independent* of frequency. This is an approximation: no system responds instantaneously to any field, but if one has a system where the lowest resonance frequency is much larger than any of the frequencies in the electric field, the system can respond approximately instantaneously. We can see this in our model of the anharmonic oscillator in which for all $\omega \ll \omega_0$.

Then $\chi(\tau_1, \cdots, \tau_n) = \epsilon_0 \chi \delta(\tau_1) \cdots \delta(\tau_n)$ and

$$P_i(t) = \epsilon_0 \chi_{ii_1 \cdots i_n} E_{i_1}(t) \cdots E_{i_n}(t). \tag{IV.1}$$

It is also clear that

$$\chi(\omega_1 \cdots \omega_n) = \chi, \tag{IV.2}$$

and so in frequency-domain, we have:

$$P_i^{(n)}(\mathbf{r}, \omega) = \epsilon_0 \int \left(\prod_{i=1}^{n} \frac{d\omega_i}{2\pi} \right) 2\pi \delta(\omega - \omega_\sigma) \chi_{ii_1 \cdots i_n}(\mathbf{r}) E_{i_1}(\mathbf{r}, \omega_i) \cdots E_{i_n}(\mathbf{r}, \omega_n). \tag{IV.3}$$

It is clear from the expressions above that the frequency-domain susceptibility for a dispersionless medium must be *real*.

Dispersionless nonlinear media have important properties.

A. Track 2: Existence of a conserved energy

A dispersionless nonlinear medium has a conserved energy. We will find that energy here. We follow a different method from Boyd which is entirely classical [9]. A number of the results we derive here are derived using quantum mechanics in Boyd.

To arrive at a conserved energy, we are going to explicitly derive a Hamiltonian for the electromagnetic field. This is done by finding a Lagrangian that reproduces

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[9] In his approach, he appeals to a quantum mechanical derivation of the nonlinear susceptibilities to show various properties of a lossless / dispersionless medium. Our opinion is that one can arrive that these properties consistently classically, and so we "prefer" our approach though it requires additional apparatus!

the equations of motion (the Maxwell equations with nonlinear polarization) and derive the corresponding Hamiltonian. We will use these results again later on. The Lagrangian which reproduces the *vacuum* Maxwell equations is (see Appendix B)

$$L = \int d\mathbf{r}\ \mathcal{L}, \text{ with } \mathcal{L} = \frac{\epsilon_0}{2}(\partial_t \mathcal{A})^2 - c^2(\nabla \times \mathbf{A})^2. \tag{IV.4}$$

The Maxwell equations are arrived at through the Euler-Lagrange equation, which is

$$\frac{\partial \mathcal{L}}{\partial \phi} - \nabla_{\mathbf{r}} \cdot \frac{\partial \mathcal{L}}{\partial(\nabla_{\mathbf{r}}\phi)} = \partial_t \frac{\partial \mathcal{L}}{\partial(\partial_t \phi)}, \tag{IV.5}$$

where ϕ refers to any component of the vector potential. For the vacuum Lagrangian, the corresponding Maxwell equation is

$$\nabla \times \nabla \times \mathbf{A} + \frac{1}{c^2}\partial_t^2 \mathbf{A} = 0, \tag{IV.6}$$

which reduces to the correct Maxwell equation in the absence of free charges by noting that $\mathbf{E} = -\partial_t \mathbf{A}$.

In the presence of nonlinear sources, the equation of motion becomes

$$\nabla \times \nabla \times \mathbf{A} + \frac{1}{c^2}\partial_t^2 \mathbf{A} = \mu_0 \mathbf{J} = \mu_0 \partial_t \mathbf{P}[-\partial_t \mathbf{A}]. \tag{IV.7}$$

We want to find a term of the Lagrangian density $\mathcal{L}_{\text{pol}}$ that produces this additional term in the equation of motion. It is not hard to guess that the term is

$$\mathcal{L}_{\text{pol}} = \epsilon_0 \sum_{n=1}^{\infty} \frac{1}{n+1} \chi^{(n)}_{i_0 i_1 i_2 \cdots i_n} E_{i_0} E_{i_1} \cdots E_{i_n} = \epsilon_0 \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n+1} \chi^{(n)}_{i_0 i_1 i_2 \cdots i_n} (\partial_t A_{i_0})(\partial_t A_{i_1}) \cdots (\partial_t A_{i_n}). \tag{IV.8}$$

This Lagrangian density contributes to the equation of motion via a term

$$\frac{\partial}{\partial(\partial_t A_i)} \mathcal{L}_{\text{pol}} = -\epsilon_0 \sum_{n=1}^{\infty} \chi^{(n)}_{i i_1 i_2 \cdots i_n} E_{i_0} E_{i_1} \cdots E_{i_n} = -P_i. \tag{IV.9}$$

In writing this, I have used the fact that the nonlinear Lagrangian density implicitly picks out the *fully symmetric* part of the susceptibility tensor. Since the Lagrangian generates dynamics, it must be the case that we can simply take the nonlinear susceptibility to be symmetric with respect to all of its indices. This is equivalent to a Kleinman symmetry [10].The resulting equation of motion is what we expect.

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[10] Note that the $n = 1$ term is the linear response, which can be included here without loss of generality.

The total Lagrangian density, including the parts that reproduce the vacuum-field Maxwell equations is

$$\mathcal{L} = \frac{\epsilon_0}{2}(\partial_t \mathcal{A})^2 - c^2(\nabla \times \mathbf{A})^2 + \mathcal{L}_{\text{pol}}. \tag{IV.10}$$

The Lagrangian can be converted to a Hamiltonian density via

$$\mathcal{H} = \frac{\partial \mathcal{L}}{\partial(\partial_t \mathbf{A})} \cdot (\partial_t \mathbf{A}) - \mathcal{L} = \frac{\epsilon_0}{2}\left(\mathbf{E}^2 + c^2\mathbf{B}^2\right) + \epsilon_0 \sum_{n=1}^{\infty} \frac{n}{n+1} \chi^{(n)}_{i_0 i_1 i_2 \cdots i_n} E_{i_0} E_{i_1} \cdots E_{i_n}. \tag{IV.11}$$

For a system with time-translation symmetry, like this one, there is a conserved energy which is simply the integral of the Hamiltonian density. We may therefore say that the conserved energy is

$$U = \int d\mathbf{r} \mathcal{H} = \epsilon_0 \int d\mathbf{r} \, \left(\frac{1}{2}\left(\epsilon \mathbf{E}^2 + c^2\mathbf{B}^2\right) + \sum_{n=2}^{\infty} \frac{n}{n+1} \chi^{(n)}_{i_0 i_1 i_2 \cdots i_n} E_{i_0} E_{i_1} \cdots E_{i_n} \right), \tag{IV.12}$$

where we have separated out the quadratic term in $\mathcal{L}_{\text{pol}}$ in order to separate the Lagrangian density into quadratic and non-quadratic parts. Occasionally, we will use a simplified notation for the nonlinear terms representing the full contraction of the nonlinear susceptibility against $(n+1)$ fields:

$$U = \int d\mathbf{r} \mathcal{H} = \epsilon_0 \int d\mathbf{r} \, \left(\frac{1}{2}\left(\epsilon \mathbf{E}^2 + c^2\mathbf{B}^2\right) + \sum_{n=2}^{\infty} \frac{n}{n+1} \chi^{(n)} : \mathbf{E}^{\otimes(n+1)} \right). \tag{IV.13}$$

Since the energy associated with the electromagnetic field is conserved, we call such a system *lossless.*

B. Kleinman symmetry

By construction of a Lagrangian $\mathcal{L}$ that reproduces the Maxwell equations, it is required by construction that the nonlinear susceptibility can be taken to be *fully* permutation symmetric with respect to its indices. This is referred to Kleinman symmetry. There is an *related* symmetry called *full permutation symmetry* which says that we can permute *any* the indices (including the first) as long as we simultaneously interchange the frequency indices. Kleinman symmetry can be seen as a special case of full permutation symmetry in which the nonlinear susceptibility is frequency-independent.

1. *Application to second-order susceptibility*

The Kleinman symmetry can be used to represent second-order nonlinear polarization in a simplified manner. Define (as has been historically done)

$$d_{ijk} = \frac{1}{2}\chi^{(2)}_{ijk}. \tag{IV.14}$$

In a lossless medium, the indices d_{ijk} is completely symmetric under any interchange of indices: it is therefore symmetric with respect to interchange of j and k. As a result, we can take $d_{ijk} \to d_{il}$ where $\ell = 1, ..., 6$ and maps to (j, k) via:

$$(1,1) \to 1, (2,2) \to 2, (3,3) \to 3, (2,3)/(3,2) \to 4, (1,3)/(3,1) \to 5, (1,2)/(2,1) \to 6. \tag{IV.15}$$

This reduced form is called *contracted notation*. Of course, we know that d_{ijk} has *full* permutation symmetry, and so these 18 components of d_{il} are not independent. There are 10 independent components [11]. The independent components can easily be found to be: $11, 12(= 26), 13(= 35), 14(= 25 = 36), 15(= 31), 16(= 21), 22, 23(= 34), 24(= 32)$ and 33.

Using contracted notation (replacing χ_{ijk} by d_{il}), we may express second-order nonlinear phenomena more compactly. For example, consider sum-frequency generation of two monochromatic waves. Assuming that we have a field [12]

$$\mathbf{E}(t) = \mathbf{E}(\omega_1)e^{-i\omega_1 t} + \mathbf{E}(\omega_2)e^{-i\omega_2 t} + \mathbf{E}(\omega_1)^* e^{i\omega_1 t} + \mathbf{E}(\omega_2)^* e^{i\omega_2 t}. \tag{IV.16}$$

The second-order polarization component at the sum-frequency is

$$P_i^{(2)}(\omega_1 + \omega_2) = 2\epsilon_0 \chi^{(2)}_{ijk} E_{1,j} E_{2,k} = 4\epsilon_0 d^{(2)}_{ijk} E_j(\omega_1) E_k(\omega_2). \tag{IV.17}$$

---

[11] Of the components of $\chi^{(2)}_{ijk}$ where all three indices are different, five of those six are redundant. Of the components where two indices are different (there are 18 such), 12 are redundant. Of components where all indices are the same, there are no such redundancies, leaving 10 out of 27 non-redundant components. Of course, it *must* be the case that d_{il} carries the same information as $\chi^{(2)}_{ijk}$ and so the number of independent quantities in either must be the same.

[12] Your instructor would have preferred to multiply this expression by 1/2 but Boyd uses the convention below. To make the resulting expressions directly comparable to the textbook, I use (begrudgingly) the convention without the 1/2.

Written in terms of contracted notation, this could be written as

$$\begin{pmatrix} P_x^{(2)}(\omega_1+\omega_2) \\ P_y^{(2)}(\omega_1+\omega_2) \\ P_z^{(2)}(\omega_1+\omega_2) \end{pmatrix} = 4\epsilon_0 \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} E_x(\omega_1)E_x(\omega_2) \\ E_y(\omega_1)E_y(\omega_2) \\ E_z(\omega_1)E_z(\omega_2) \\ E_y(\omega_1)E_z(\omega_2) + E_z(\omega_1)E_y(\omega_2) \\ E_x(\omega_1)E_z(\omega_2) + E_z(\omega_1)E_x(\omega_2) \\ E_x(\omega_1)E_y(\omega_2) + E_y(\omega_1)E_x(\omega_2) \end{pmatrix} . \tag{IV.18}$$

Written in terms of independent components of the contracted d "tensor", we could write:

$$\begin{pmatrix} P_x^{(2)}(\omega_1+\omega_2) \\ P_y^{(2)}(\omega_1+\omega_2) \\ P_z^{(2)}(\omega_1+\omega_2) \end{pmatrix} = 4\epsilon_0 \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{16} & d_{22} & d_{23} & d_{24} & d_{14} & d_{12} \\ d_{15} & d_{24} & d_{33} & d_{23} & d_{13} & d_{14} \end{pmatrix} \begin{pmatrix} E_x(\omega_1)E_x(\omega_2) \\ E_y(\omega_1)E_y(\omega_2) \\ E_z(\omega_1)E_z(\omega_2) \\ E_y(\omega_1)E_z(\omega_2) + E_z(\omega_1)E_y(\omega_2) \\ E_x(\omega_1)E_z(\omega_2) + E_z(\omega_1)E_x(\omega_2) \\ E_x(\omega_1)E_y(\omega_2) + E_y(\omega_1)E_x(\omega_2) \end{pmatrix} . \tag{IV.19}$$

For second-harmonic generation, it is relatively straightforward to see that

$$\begin{pmatrix} P_x^{(2)}(2\omega) \\ P_y^{(2)}(2\omega) \\ P_z^{(2)}(2\omega) \end{pmatrix} = 2\epsilon_0 \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{16} & d_{22} & d_{23} & d_{24} & d_{14} & d_{12} \\ d_{15} & d_{24} & d_{33} & d_{23} & d_{13} & d_{14} \end{pmatrix} \begin{pmatrix} E_x^2(\omega) \\ E_y^2(\omega) \\ E_z^2(\omega) \\ 2E_y(\omega)E_z(\omega) \\ 2E_x(\omega)E_z(\omega) \\ 2E_x(\omega)E_y(\omega) \end{pmatrix} . \tag{IV.20}$$

C. Effective value of d: d_{eff}

It is sometimes useful to recast the relations for field and polarization as scalar relations. For example, it is possible to write for sum-frequency generation

$$P(\omega_1+\omega_2) = 4\epsilon_0 d_{\text{eff}} E(\omega_1)E(\omega_2), \tag{IV.21}$$

where $P = |\mathbf{P}|, E = |\mathbf{E}|$. The effective d value depends on the exact symmetries of d_{il}. For example, as Boyd describes, for the $3m$ crystal class,

$$d_{\text{eff}} = d_{31} \sin\theta - d_{22} \cos\theta \sin(3\phi), \tag{IV.22}$$

when the two lower-frequency waves have the same polarization, where θ is the angle between the propagation direction and the crystal axis (defined to be the z direction). ϕ is the angle between the propagation vector and the xz crystalline plane.