Chapter 1

The Nonlinear Optical Susceptibility

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. The beginning of the field of nonlinear optics is often taken to be the discovery of second-harmonic generation by Franken et al. (1961), shortly after the demonstration of the first working laser by Maiman in 1960. Nonlinear optical phenomena are “nonlinear” in
\[ \tilde{P}(t) = \varepsilon_0 \left[ \chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \cdots \right] \]

\[ \equiv \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \cdots . \] (1.1.2)

- Assuming \( P(t) \) depends only on \( E(t) \), i.e. instantaneous response.
- This implies through Kramer-Kronig relation (discussed later) that we are assuming no loss and no dispersion. Not generally true.
- We will see that

\[ \tilde{P}^{(1)}(t) = \varepsilon_0 \int_0^\infty R^{(1)}(\tau) \tilde{E}(t - \tau) d\tau. \]
Rough Estimates of Nonlinear Coefficients

\[ \tilde{P}(t) = \epsilon_0 [\chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \cdots ] \]
\[ \equiv \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \cdots . \]  

- When \( E \sim E_{\text{atomic}} = e / K a_B^2 \), the nonlinear terms \( \sim \) linear terms

\[ a_B = K \hbar^2 / me^2 ; K = 4\pi \varepsilon_0 / \omega ; E_{\text{at}} \sim 5 \times 10^{11} \frac{V}{m} = 0.5 \frac{V}{pm} \]

In comparison, peak field in our pulsed laser is \( \sim 1 \text{mJ/100fs} \) over say 2\( \mu \text{m} \) diameter beam has \( E \sim 0.15 \frac{V}{pm} \)

- So \( \chi^{(1)} \sim E_{\text{at}}^{(2)} \); \( \chi^{(1)} \sim 1 \) then \( \chi^{(2)} \sim 2 \text{ pm/V} \)

- So \( \chi^{(1)} \sim E_{\text{at}}^{(3)} \); \( \chi^{(1)} \sim 1 \) then \( \chi^{(3)} \sim 4 \text{ pm}^2 / \text{V}^2 \)
Second Harmonic Generation

\[ \tilde{E}(t) = E e^{-i\omega t} + \text{c.c.} \]

\[ \tilde{P}^{(2)}(t) = \varepsilon_0 \chi^{(2)} \tilde{E}^2(t) \]

\[ \tilde{P}^{(2)}(t) = 2\varepsilon_0 \chi^{(2)} EE^* + (\varepsilon_0 \chi^{(2)} E^2 e^{-i2\omega t} + \text{c.c.}). \]  

(1.2.2)

The solid line in the figure represents the atomic ground state, and the dashed lines represent what are known as virtual levels. **These levels are not energy eigenlevels of the free atom but rather represent the combined energy of one of the energy eigenstates of the atom and of one or more photons of the radiation field.**
Sum and Difference Frequency Generation with $\chi^{(2)}$

\[ P(\omega_1 + \omega_2) = 2\epsilon_0 \chi^{(2)} E_1 E_2. \]

\[ P(\omega_1 - \omega_2) = 2\epsilon_0 \chi^{(2)} E_1 E_2^*. \]
Sum and Difference Frequency Generation with $\chi^{(2)}$

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + \text{c.c.}$$

$$\tilde{P}^{(2)}(t) = \varepsilon_0 \chi^{(2)}(\tilde{E}(t))^2,$$

$$\tilde{P}^{(2)}(t) = \varepsilon_0 \chi^{(2)}\left[ E_1^2 e^{-2i\omega_1 t} + E_2^2 e^{-2i\omega_2 t} + 2E_1 E_2 e^{-i(\omega_1 + \omega_2) t} + 2\varepsilon_0 \chi^{(2)}[ E_1 E_1^* + E_2 E_2^*] \right].$$

$$\tilde{P}^{(2)}(t) = \sum_{n} P(\omega_n) e^{-i\omega_n t},$$

where the summation extends over positive and negative frequencies $\omega_n$.

$$P(2\omega_1) = \varepsilon_0 \chi^{(2)} E_1^2 \quad \text{(SHG)},$$

$$P(2\omega_2) = \varepsilon_0 \chi^{(2)} E_2^2 \quad \text{(SHG)},$$

$$P(\omega_1 + \omega_2) = 2\varepsilon_0 \chi^{(2)} E_1 E_2 \quad \text{(SFG)},$$

$$P(\omega_1 - \omega_2) = 2\varepsilon_0 \chi^{(2)} E_1 E_2^* \quad \text{(DFG)},$$

$$P(0) = 2\varepsilon_0 \chi^{(2)} (E_1 E_1^* + E_2 E_2^*) \quad \text{(OR)}.$$
Third Order Nonlinearity, $\chi^{(3)}$

\[ \tilde{P}^{(3)}(t) = \epsilon_0 \chi^{(3)} \tilde{E}(t)^3. \]

\[ \tilde{E}(t) = \mathcal{E} \cos \omega t. \]

\[ \tilde{P}^{(3)}(t) = \frac{1}{4} \epsilon_0 \chi^{(3)} \mathcal{E}^3 \cos 3\omega t + \frac{3}{4} \epsilon_0 \chi^{(3)} \mathcal{E}^3 \cos \omega t. \]

\( n = n_0 + n_2 I, \)

**Figure 1.2.5** Third-harmonic generation.

**Figure 1.2.6** Self-focusing of light.
Third Order Nonlinearity, $\chi^{(3)}$: General Case

$$\tilde{P}^{(3)}(t) = \epsilon_0 \chi^{(3)} \tilde{E}^3(t) = \sum_{n} P(\omega_n) e^{-i\omega_n t},$$

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + E_3 e^{-i\omega_3 t} + c.c.$$
Third Order Nonlinearity, $\chi^{(3)}$: Two Examples

(a)

$\omega_1 \rightarrow \chi^{(3)} \rightarrow \omega_4 = \omega_1 + \omega_2 + \omega_3$

(b)

$\omega_1 \rightarrow \chi^{(3)} \rightarrow \omega_4 = \omega_1 + \omega_2 - \omega_3$
Optical Parametric Oscillator

\[ \omega_1 = \omega_2 + \omega_3 \]
(pump)

\[ \chi^{(2)} \]

\[ \omega_2 \text{ (signal)} \]

\[ \omega_3 \text{ (idler)} \]

**Figure 1.2.4** The optical parametric oscillator. The cavity end mirrors have high reflectivities at frequencies \( \omega_2 \) and/or \( \omega_3 \). The output frequencies can be tuned by means of the orientation of the crystal.
Parametric vs. Non-Parametric Processes

but the word parametric has come to denote a process in which the initial and final quantum-mechanical states of the system are identical. Consequently, in a parametric process population can be removed from the ground state only for those brief intervals of time when it resides in a virtual level. According to the uncertainty principle, population can reside in a virtual level for a time interval of the order of $\hbar/\delta E$, where $\delta E$ is the energy difference between the virtual level and the nearest real level. Conversely, processes that do involve the transfer of population from one real level to another are known as non-parametric processes. The processes that we describe in the remainder of the present section are all examples of nonparametric processes.

One difference between parametric and nonparametric processes is that parametric processes can always be described by a real susceptibility; conversely, nonparametric processes are described by a complex susceptibility by means of a procedure described in the following section. Another difference is that photon energy is always conserved in a parametric process; photon energy need not be conserved in a nonparametric process, because energy can be transferred to or from the material medium. For this reason, photon energy level diagrams of the sort shown in Figs. 1.2.1, 1.2.2, 1.2.3, 1.2.5, and 1.2.7 to describe parametric processes play a less definitive role in describing nonparametric processes.
Non-Parametric Processes: Examples

Saturable Absorber

\[ \alpha = \frac{\alpha_0}{1 + I/I_s}, \]

Two-photon absorption

\[ \omega \]

\[ \omega \]

\[ \omega = \omega - \omega_v \]

\[ \omega_v \]

FIGURE 1.2.8 Bistable optical device.

FIGURE 1.2.10 Two-photon absorption.

Stimulated Raman Scattering

\[ \omega \]

\[ \omega = \omega - \omega_v \]

\[ \omega_v \]

FIGURE 1.2.9 Typical input-versus-output characteristics of a bistable optical device.

FIGURE 1.2.11 Stimulated Raman scattering.
Classical theory of Nonlinear Optics, 1/7

\[ \tilde{F}_{\text{restoring}} = -m\omega_0^2\ddot{x} - ma\dot{x}^2, \]

\[ U(\ddot{x}) = -\int \tilde{F}_{\text{restoring}} d\ddot{x} = \frac{1}{2}m\omega_0^2\dot{x}^2 + \frac{1}{3}ma\ddot{x}^3. \]

\[ \ddot{x} + 2\gamma \dot{x} + \omega_0^2\ddot{x} + a\dot{x}^2 = -\lambda e\tilde{E}(t)/m. \]

\textbf{FIGURE 1.4.1} Potential energy function for a noncentrosymmetric medium.

\( \lambda \) is a parameter that ranges continuously between zero and one and that will be set equal to one at the end of the calculation. The expansion parameter \( \lambda \) thus characterizes the strength of the perturbation.
Classical theory of Nonlinear Optics, 2/7

\[ \ddot{x} + 2\gamma \dot{x} + \omega_0^2 x + a \ddot{x}^2 = -\lambda e \ddot{E}(t)/m. \]

\[ \ddot{x} = \lambda \dddot{x}^{(1)} + \lambda^2 \ddot{x}^{(2)} + \lambda^3 \dot{x}^{(3)} + \cdots. \]

\[ \dddot{x}^{(1)} + 2\gamma \ddot{x}^{(1)} + \omega_0^2 \dot{x}^{(1)} = -e \ddot{E}(t)/m, \quad \leftrightarrow \quad \chi^{(1)} \]

\[ \dddot{x}^{(2)} + 2\gamma \ddot{x}^{(2)} + \omega_0^2 \dot{x}^{(2)} + a [\dddot{x}^{(1)}]^2 = 0, \quad \leftrightarrow \quad \chi^{(2)} \]

\[ \dddot{x}^{(3)} + 2\gamma \ddot{x}^{(3)} + \omega_0^2 \dot{x}^{(3)} + 2a \ddot{x}^{(1)} \dddot{x}^{(2)} = 0, \quad \text{etc.} \quad \leftrightarrow \quad \chi^{(3)} \]
\[
\ddot{x}^{(1)} + 2\gamma \dot{x}^{(1)} + \omega_0^2 x^{(1)} = -e \tilde{E}(t)/m,
\]

\[x^{(1)}(\omega_j) = -\frac{e}{m} \frac{E_j}{D(\omega_j)},\]

\[D(\omega_j) = \omega_0^2 - \omega_j^2 - 2i\omega_j\gamma.\]
Let 
\[
\tilde{x}^{(1)}(t) = x^{(1)}(\omega_1)e^{-i\omega_1 t} + x^{(1)}(\omega_2)e^{-i\omega_2 t} + c.c.,
\]
\[
\tilde{x}^{(1)}(\omega_j) = -\frac{e}{m} \frac{E_j}{D(\omega_j)},
\]
\[
x^{(2)}(2\omega_1) = \frac{-a(e/m)^2 E_1^2}{D(2\omega_1) D^2(\omega_1)},
\]
\[
x^{(2)}(2\omega_2) = \frac{-a(e/m)^2 E_2^2}{D(2\omega_2) D^2(\omega_2)},
\]
\[
x^{(2)}(\omega_1 + \omega_2) = \frac{-2a(e/m)^2 E_1 E_2}{D(\omega_1 + \omega_2) D(\omega_1) D(\omega_2)},
\]
\[
x^{(2)}(\omega_1 - \omega_2) = \frac{-2a(e/m)^2 E_1 E_2^*}{D(\omega_1 - \omega_2) D(\omega_1) D(-\omega_2)},
\]
\[
x^{(2)}(0) = \frac{-2a(e/m)^2 E_1 E_1^*}{D(0) D(\omega_1) D(-\omega_1)} + \frac{-2a(e/m)^2 E_2 E_2^*}{D(0) D(\omega_2) D(-\omega_2)}.\]
\[ \chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2) = \frac{N(e^3/m^2)a}{\varepsilon_0 D(\omega_1 + \omega_2)D(\omega_1)D(\omega_2)}, \]

\[ = \frac{\varepsilon_0^2 ma}{N^2 e^3} \chi^{(1)}(\omega_1 + \omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(\omega_2). \]

**Miller’s Rule**

\[ \frac{\chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2)}{\chi^{(1)}(\omega_1 + \omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(\omega_2)} = \frac{ma\varepsilon_0^2}{N^2 e^3} \quad \sim \text{constant for all noncentrosymmetric materials} \]
Estimating $\chi^{(2)}$ from Lorentz Model, 6/7

$$\chi^{(2)}(\omega_1 + \omega_2, \omega_1, \omega_2) = \frac{N(e^3/m^2)a}{\epsilon_0 D(\omega_1 + \omega_2) D(\omega_1) D(\omega_2)},$$

Estimates

$\tilde{F}_{\text{restoring}} = -m\omega_0^2 \ddot{x} - ma\dot{x}^2,$

$$m\omega_0^2 d = mad^2 \quad \Rightarrow \quad a = \frac{\omega_0^2}{d}.$$ 

$d$ is $\sim$ half the lattice constant

$$D(\omega_j) = \omega_0^2 - \omega_j^2 - 2i\omega_j\gamma \sim \omega_0^2$$

$N \sim 1/d^3$

$\Rightarrow \quad \chi^{(2)} = \frac{e^3}{\epsilon_0 m^2 \omega_0^4 d^4} \simeq 6.9 \times 10^{-12}$ m/V,
Classical Model for Nonlinearities, 7/7

\[ \chi^{(2)}(\omega_1 - \omega_2, \omega_1, -\omega_2) = \frac{N(e^3/\varepsilon_0 m^2)a}{D(\omega_1 - \omega_2)D(\omega_1)D(-\omega_2)} \]

\[ = \frac{\varepsilon_0^2 ma}{N^2 e^3} \chi^{(1)}(\omega_1 - \omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(-\omega_2), \]

\[ \chi^{(2)}(0, \omega_1, -\omega_1) = \frac{N(e^3/m^2)a}{\varepsilon_0 D(0)D(\omega_1)D(-\omega_1)} \]

\[ = \frac{\varepsilon_0^2 ma}{N^2 e^3} \chi^{(1)}(0) \chi^{(1)}(\omega_1) \chi^{(1)}(-\omega_1). \]

\[ \chi^{(3)}_{ijkl}(\omega_q, \omega_m, \omega_n, \omega_p) = \frac{b m e_0^3}{3 N^3 e^4} \left[ \chi^{(1)}(\omega_q) \chi^{(1)}(\omega_m) \chi^{(1)}(\omega_n) \chi^{(1)}(\omega_p) \right] \]

\[ \times [\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}]. \quad (1.4) \]
\[ P_i(\omega_n + \omega_m) = \varepsilon_0 \sum_{jk} \sum_{(nm)} \chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m), \]

\[ \omega_3 = \omega_1 + \omega_2 \]

\[ \begin{align*}
\chi_{ijk}^{(2)}(\omega_1, \omega_3, -\omega_2), & \quad \chi_{ijk}^{(2)}(\omega_1, -\omega_2, \omega_3), & \quad \chi_{ijk}^{(2)}(\omega_2, \omega_3, -\omega_1), \\
\chi_{ijk}^{(2)}(\omega_2, -\omega_1, \omega_3), & \quad \chi_{ijk}^{(2)}(\omega_3, \omega_1, \omega_2), & \quad \text{and} \quad \chi_{ijk}^{(2)}(\omega_3, \omega_2, \omega_1), \\
\chi_{ijk}^{(2)}(\bar{\omega}_1, \bar{\omega}_3, +\omega_2), & \quad \chi_{ijk}^{(2)}(\bar{\omega}_1, +\omega_2, \bar{\omega}_3), & \quad \chi_{ijk}^{(2)}(\bar{\omega}_2, \bar{\omega}_3, +\omega_1), \\
\chi_{ijk}^{(2)}(\bar{\omega}_2, +\omega_1, \bar{\omega}_3), & \quad \chi_{ijk}^{(2)}(\bar{\omega}_3, \bar{\omega}_1, \bar{\omega}_2), & \quad \text{and} \quad \chi_{ijk}^{(2)}(\bar{\omega}_3, \bar{\omega}_2, \bar{\omega}_1) 
\end{align*} \]

12 tensors x 27 terms per tensor = 324 complex terms!
Symmetries of Nonlinear Optical Tensors

- Reality of the fields
- Intrinsic permutation symmetry
- Symmetries for lossless media:
  - $\chi^{(2)}$ are all real
  - Full permutation symmetry
- Kleinman’s symmetry for lossless and dispersionless media
- Crystallographic symmetry
Symmetries 1: Realities of the Fields and Polarization

\[ \tilde{P}^{(3)}(t) = \sum_{n} \tilde{P}(\omega_n)e^{-i\omega_n t} \quad \text{and} \quad \tilde{E}(t) = \sum_{n} \tilde{E}(\omega_n)e^{-i\omega_n t} \]

If \( \tilde{P} \) and \( \tilde{E} \) are both real, then

\[ P(-\omega_n) = P(\omega_n)^* \quad \text{and} \quad E(-\omega_n) = E(\omega_n)^* \]

\[ \Rightarrow \quad \chi^{(2)}_{ijk}(-\omega_n - \omega_m, -\omega_n, -\omega_m) = \chi^{(2)}_{ijk}(\omega_n + \omega_m, \omega_n, \omega_m)^* \]
Symmetries 2: Intrinsic Permutation Symmetry

\[ \chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) = \chi_{ikj}^{(2)}(\omega_n + \omega_m, \omega_m, \omega_n). \]

This property is known as intrinsic permutation symmetry. More physically, this condition is simply a statement that it cannot matter which is the first field and which is the second field in products such as \( E_j(\omega_n)E_k(\omega_m) \).
Symmetries 3a: For Lossless Media

The first of these conditions states that for a lossless medium all of the components of $\chi^{(2)}_{ijk}(\omega_n + \omega_m, \omega_n, \omega_m)$ are real.
Symmetries 3b for Lossless Media: Full permutation symmetry

This condition states that all of the frequency arguments of the nonlinear susceptibility can be freely interchanged, as long as the corresponding Cartesian indices are interchanged simultaneously.

\[ \chi_{ijk}^{(2)}(\omega_3 = \omega_1 + \omega_2) = \chi_{jki}^{(2)}(-\omega_1 = -\omega_2 - \omega_3) = \chi_{jki}^{(2)}(-\omega_1 = -\omega_2 + \omega_3)^* = \chi_{jki}^{(2)}(\omega_1 = -\omega_2 + \omega_3) \]

\[ \chi_{ijk}^{(2)}(\omega_3 = \omega_1 + \omega_2) = \chi_{jki}^{(2)}(\omega_1 = -\omega_2 + \omega_3) = \chi_{kij}^{(2)}(\omega_2 = \omega_3 - \omega_1) \]

In a lossless medium, it doesn’t matter which two frequencies come in to generate the third frequency.
Symmetries 4 for Lossless & Dispersionless Media: Kleinman’s symmetry

However, under the present conditions $\chi^{(2)}$ does not actually depend on the frequencies, and we can therefore permute the indices without permuting the frequencies, leading to the result

$$\chi_{ijk}^{(2)}(\omega_3 = \omega_1 + \omega_2) = \chi_{jki}^{(2)}(\omega_1 = -\omega_2 + \omega_3) = \chi_{kij}^{(2)}(\omega_2 = \omega_3 - \omega_1)$$

$$= \chi_{ikj}^{(2)}(\omega_3 = \omega_2 + \omega_1) = \chi_{kji}^{(2)}(\omega_2 = -\omega_1 + \omega_3)$$

$$= \chi_{jik}^{(2)}(\omega_1 = \omega_3 - \omega_2).$$

Intrinsic permutation
+ Full permutation

Intrinsic permutation
+ Full permutation
+ Kleinman’s
Symmetries 5a under Spatial Inversion Symmetry

\[ \tilde{P}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t) \]

\[ -\tilde{P}(t) = \epsilon_0 \chi^{(2)} \left[ -\tilde{E}(t) \right]^2 \]

\[ \chi^{(2)} = 0 \]

All odd-rank polar tensors are zero when spatial inversion is present.

Figure 1.5.2: Waveforms associated with the atomic response.
Symmetries 5b: Neumann's Principle

**Biaxial crystal classes**

- class 1
- class \( m \)
- class \( mm \)

**Uniaxial crystal classes**

- class 3
- class \( 3 \)

**Uniaxial crystal classes (Continued)**

- classes 6 and 4
- classes 6mm and 4mm

**Isotropic crystal classes**

- classes \( \bar{4}3m \) and 23
- class 432 (all elements vanish)

**Figure 1.5.3** Form of the \( d_{ij} \) matrix for the 21 crystal classes that lack inversion symmetry. Small dot: zero coefficient; large dot: nonzero coefficient; square: coefficient that is zero when Kleinman's symmetry condition is valid; connected symbols: numerically equal coefficients, but the open-symbol coefficient is opposite in sign to the closed symbol to which it is joined. Dashed connections are valid only under Kleinman's symmetry conditions. (After Zernike and Midwinter, 1973.)
The Time Domain Analysis of the Linear Optical Response

$$\tilde{P}^{(1)}(t) = \varepsilon_0 \int_{0}^{\infty} R^{(1)}(\tau) \tilde{E}(t - \tau) \, d\tau.$$  

Here $R^{(1)}(\tau)$ is the linear response function, which gives the contribution to the polarization produced at time $t$ by an electric field applied at the earlier time $t - \tau$. The total polarization is obtained by integrating these contributions over all previous times $\tau$. In writing Eq. (1.6.1) as shown, with the lower limit of integration set equal to zero and not to $-\infty$, we have assumed that $R^{(1)}(\tau)$ obeys the causality condition $R^{(1)}(\tau) = 0$ for $\tau < 0$. This condition expresses the fact that $\tilde{P}^{(1)}(t)$ depends only on past and not on future values of $\tilde{E}(t)$.

$$\tilde{P}^{(1)}(t) = \varepsilon_0 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \chi^{(1)}(\omega; \omega) E(\omega) e^{-i\omega t} = \varepsilon_0 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \int_{0}^{\infty} d\tau R^{(1)}(\tau) e^{i\omega \tau} E(\omega) e^{-i\omega t}$$

$$\chi^{(1)}(\omega; \omega) = \int_{0}^{\infty} d\tau R^{(1)}(\tau) e^{i\omega \tau}.$$
Time Domain Analysis of the Nonlinear Response

\[ \tilde{P}^{(2)}(t) = \varepsilon_0 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 R^{(2)}(\tau_1, \tau_2)E(t - \tau_1)E(t - \tau_2). \]

\[ = \varepsilon_0 \int_{-\infty}^\infty \frac{d\omega_1}{2\pi} \int_{-\infty}^\infty \frac{d\omega_2}{2\pi} \chi^{(2)}(\omega_\sigma; \omega_1, \omega_2)E(\omega_1)E(\omega_2)e^{-i\omega_\sigma t}, \]

\[ \chi^{(2)}(\omega_\sigma; \omega_1, \omega_2) = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 R^{(2)}(\tau_1, \tau_2)e^{i(\omega_1 \tau_1 + \omega_2 \tau_2)} \]

\[ \chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3) = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \]

\[ \times R^{(3)}(\tau_1, \tau_2, \tau_3) e^{i(\omega_1 \tau_1 + \omega_2 \tau_2 + \omega_3 \tau_3)} \]
Kramer-Kronig Relationship

To summarize the results of this section, we have seen that Kramers–Kronig relations, which are always valid in linear optics, are valid for some but not all nonlinear optical processes.

\[
\chi^{(1)}(\omega) = \frac{-i}{\pi} \int_{-\infty}^{\infty} \frac{\chi^{(1)}(\omega')}{\omega' - \omega} d\omega'.
\]

\[
\text{Im} \chi^{(1)}(\omega) = \frac{-2\omega}{\pi} \int_{0}^{\infty} \frac{\text{Re} \chi^{(1)}(\omega')}{\omega'^2 - \omega^2} d\omega'.
\]

\[
\text{Re} \chi^{(1)}(\omega) = \frac{2}{\pi} \int_{0}^{\infty} \frac{\omega' \text{Im} \chi^{(1)}(\omega')}{\omega'^2 - \omega^2} d\omega'.
\]

\[
\chi^{(2)}(2\omega; \omega, \omega) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(2)}(2\omega'; \omega', \omega')}{\omega' - \omega} d\omega'.
\]

\[
\chi^{(3)}(3\omega; \omega, \omega, \omega) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(3)}(3\omega'; \omega', \omega', \omega')}{\omega' - \omega} d\omega'.
\]

\[
\chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(3)}(\omega'_\sigma; \omega_1, \omega'_2, \omega_3)}{\omega'_2 - \omega_2} d\omega'_2
\]

Probably the most important process for which it is not possible to form a Kramers–Kronig relation is for the self-induced change in refractive index, that is, for processes described by the nonlinear susceptibility \(\chi^{(3)}(\omega; \omega, \omega, -\omega)\). Note that this susceptibility is not of the form...