Chapter 2 Macroscopic Theory of Optical Susceptibility Tensors

Purpose of this chapter

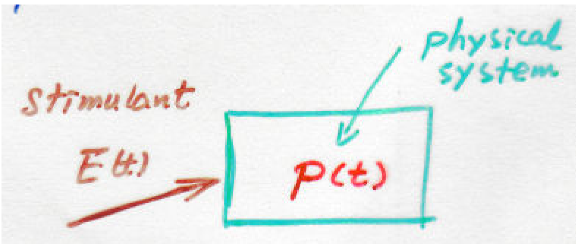
Use a few simple physical principles to deduce important fundamental and universal properties of nonlinear optical susceptibilities.

We will start from $\boldsymbol{P}(t) \leftrightarrow \boldsymbol{E}(\tau)$ **Constitutive Relation** via the following two Approaches:

(1) From time-domain $\Rightarrow$ Response Function

(2) From frequency-domain $\Rightarrow$ Susceptibility

2.1 Response Function and Constitutive Relations



In general, any intuitive picture given shall reveal ***P***(t) to be nonlocal and a finite response time. But for simplicity, let us first consider

- **Local Response** [Note that this limitation can be lifted with spatial dispersion of $\boldsymbol{\chi}(\vec{\boldsymbol{k}},\boldsymbol{\omega})$ as in the last section of this chapter]

  We assume polarization at a position in the medium is determined completely by the electric field at that position, *i.e.*, $\vec{P}_\omega(\vec{r}) = \vec{P}_\omega[\vec{E}(\vec{r})] \simeq \vec{\chi}^{(1)}(\omega)\vec{E}_\omega(\vec{r})$.

- Invoking **time-invariance**

  Dynamical properties of the system are assumed to be unchanged by a translation of the time origin, that is, $R^{(1)}(t_1+\tau;t_1) = R^{(1)}(t_2+\tau;t_2) = R^{(1)}(\tau;0)$

  Time-displacement of the driving electric field merely results in a corresponding time-displacement of the induced polarization.

2.1.1 Linear Response

Starting from $P^{(1)}(t) = [\varepsilon_0]\int_{-\infty}^{+\infty} T^{(1)}(t;\tau)E(\tau)\,d\tau$. (1)

Here $T^{(1)}(t;\tau)$ is a 2nd rank tensor. Let us

- first perform a time displacement $t \to t + t_0$

Eq. (1) then becomes $P^{(1)}(t+t_0) = \int_{-\infty}^{+\infty} T^{(1)}(t+t_0;\tau)E(\tau)\,d\tau$. (2)

- Then invoking time-invariance principle on Eq. (1): $P(t+t_0) \leftrightarrow E(\tau+t_0)$

$$P^{(1)}(t+t_0) = \int_{-\infty}^{+\infty} T^{(1)}(t;\tau)E(\tau+t_0)\,d\tau$$

Let $\tau' = \tau + t_0$, $P^{(1)}(t+t_0) = \int_{-\infty}^{+\infty} T^{(1)}(t;\tau'-t_0)E(\tau')\,d\tau'$ (3)

Compare Eq. (2) and Eq. (3), we obtain $T^{(1)}(t+t_0;\tau) = T^{(1)}(t;\tau-t_0)$.

i.e., $T^{(1)}(t;\tau)$ **depends on $t-\tau$ only, not on their individual values**.

Let t=0 and $t_0 \to t$, then $T^{(1)}(t;\tau) = T^{(1)}(0;\tau-t) \equiv R^{(1)}(t-\tau)$, defining a linear polarization response function of the medium $R^{(1)}(t-\tau)$ and

$$P^{(1)}(t) = \int_{-\infty}^{+\infty} R^{(1)}(t-\tau)E(\tau)\,d\tau$$

Two important aspects of $R^{(1)}$:

- **Causality condition**: $R^{(1)}(t) = 0$ when $t < 0$.
- **Reality condition**: $R^{(1)}(t)$ is a real function of t. Both $P^{(1)}(t)$ and $E(t)$ are real, since they are physical quantities.

2.1.2 Quadratic Nonlinear Response

Starting from $P_\mu^{(2)}(t) = \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2\, T_{\mu\alpha\beta}^{(2)}(t;\tau_1,\tau_2)E_\alpha(\tau_1)E_\beta(\tau_2)$. (4)

Here $T_{\mu\alpha\beta}^{(2)}$ is a 3rd rank tensor.

Note that $T_{\mu\alpha\beta}^{(2)}(t;\tau_1,\tau_2)$ uniquely determines the quadratic polarization in the NLO medium. However, because of the quadratic form of Eq. (4), $T_{\mu\alpha\beta}^{(2)}$ is not uniquely determined by Eq. (4). This can be seen from

$T_{\mu\alpha\beta}^{(2)}(t;\tau_1,\tau_2) = S_{\mu\alpha\beta}^{(2)}(t;\tau_1,\tau_2) + A_{\mu\alpha\beta}^{(2)}(t;\tau_1,\tau_2)$ where

$S_{\mu\alpha\beta}^{(2)}(t;\tau_1,\tau_2) = \frac{1}{2}[T_{\mu\alpha\beta}^{(2)}(t;\tau_1,\tau_2) + T_{\mu\beta\alpha}^{(2)}(t;\tau_2,\tau_1)]$ and

$$A_{\mu\alpha\beta}{}^{(2)}(t;\tau_1,\tau_2)=\frac{1}{2}[T_{\mu\alpha\beta}{}^{(2)}(t;\tau_1,\tau_2)-T_{\mu\beta\alpha}{}^{(2)}(t;\tau_2,\tau_1)].$$

Since an exchange of ($\alpha\,\tau_1$) and ($\beta\,\tau_2$) in Eq. (4) leaves the expression unchanged. Thus, $A_{\mu\alpha\beta}{}^{(2)}(t;\tau_1,\tau_2)$ makes no contribution to $P_\mu^{(2)}(t)$. To make $T_{\mu\alpha\beta}{}^{(2)}(t;\tau_1,\tau_2)$ unique, we must first transform it into a symmetric form by letting $A_{\mu\alpha\beta}{}^{(2)}(t;\tau_1,\tau_2)$ =0, *i.e.*,

$$T_{\mu\alpha\beta}{}^{(2)}(t;\tau_1,\tau_2)=T_{\mu\beta\alpha}{}^{(2)}(t;\tau_2,\tau_1).$$

Now by invoking

- **Time-invariance principle**

$T^{(2)}(t+t_0;\tau_1,\tau_2)=T^{(2)}(t;\tau_1-t_0,\tau_2-t_0)$ and let t =0, $t_0\to t$, we obtain

$T^{(2)}(t;\tau_1,\tau_2)\equiv R^{(2)}(t-\tau_1,t-\tau_2)$ =Quadratic Polarization Response Function.

$$P^{(2)}(t)=\int_{-\infty}^{+\infty}d\tau_1\int_{-\infty}^{+\infty}d\tau_2 R^{(2)}(t-\tau_1,t-\tau_2):E(\tau_1)E(\tau_2) \qquad (5)$$

Two important aspects of $R^{(2)}{}_{\mu\alpha\beta}(t_1,t_2)$:

- **<u>Causality condition</u>**: $R^{(2)}(t_1,t_2)$ =0 when $t_1<0$ **or** $t_2<0$.
- **<u>Reality condition</u>**: $R^{(2)}(t_1,t_2)$ is a real function of t_1 **or** t_2.
- **<u>Intrinsic Permutation Symmetry</u>**: $R^{(2)}{}_{\mu\alpha\beta}(t_1,t_2)=R^{(2)}{}_{\mu\beta\alpha}(t_2,t_1)$

2.1.3 Higher-Order Nonlinear Response

Generalize to $P^{(n)}(t)=\int_{-\infty}^{+\infty}d\tau_1\cdots\int_{-\infty}^{+\infty}d\tau_n\, T^{(n)}(t;\tau_1,\tau_2\cdots,\tau_n)\,|\,E(\tau_1)E(\tau_2)\cdots E(\tau_n)$

Here $T_{\mu\alpha_1\alpha_2\cdots\alpha_n}{}^{(n)}$ is a (***n*+1**)*th* rank tensor.

Here $T_{\mu\alpha_1\alpha_2\cdots\alpha_n}{}^{(n)}(t;\tau_1,\tau_2\cdots,\tau_n)=\frac{1}{n!}S\,T_{\mu\alpha_1\alpha_2\cdots\alpha_n}{}^{(n)}(t;\tau_1,\tau_2\cdots,\tau_n)$ with a symmetrized operator S denoting a summation over all the tensor components obtained by making the $n!$ permutations of the n pairs ($\alpha_1\tau_1$)…..($\alpha_n\tau_n$). This symmetrized operation makes $T^{(n)}$ satisfies intrinsic permutation symmetry.

$$T_{\mu\alpha_1\alpha_2\cdots\alpha_n}{}^{(n)}(t;\tau_1,\tau_2\cdots,\tau_n)\equiv R_{\mu\alpha_1\alpha_2\cdots\alpha_n}{}^{(n)}(t-\tau_1,t-\tau_2\cdots,t-\tau_n).$$

Therefore,

$$P^{(n)}(t)=\int_{-\infty}^{+\infty}d\tau_1\cdots\int_{-\infty}^{+\infty}d\tau_n\ R^{(n)}(t-\tau_1,t-\tau_2\cdots,t-\tau_n)\,|\,E(\tau_1)E(\tau_2)\cdots E(\tau_n) \qquad (6)$$

2.2 Susceptibility Tensors in the Frequency Domain

The response function in time domain can be transformed into susceptibility tensor in frequency domain.

2.2.1 The Complex Frequency Plane

$$E(\tau)\equiv\int_{-\infty}^{+\infty}E(\omega)e^{-i\omega\tau}d\omega \quad \textbf{where}$$

Note .

$$E(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}E(\tau)e^{i\omega\tau}d\tau$$

If $E(\tau)$ vanishes in the past ($\tau<0$), let $\omega=x+iy$ for mathematical convenience,

$$E(\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}E(\tau)e^{i\omega\tau}d\tau=\frac{1}{2\pi}\int_{0}^{+\infty}E(\tau)e^{(ix-y)\tau}d\tau \quad \text{exists,} \quad \text{if } y>0.$$

The integration converges if y>0 (*i.e.*, ω lies in the upper half plane. Let $d\omega\to dx$ with integration path along the real axis in the upper half-plane.

$\int_{-\infty}^{+\infty}E(\omega)e^{-i\omega\tau}d\omega$ is finite and therefore exists!

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty}dx\int_{-\infty}^{+\infty}d\tau\,E(\tau)e^{-y(\tau-t)}e^{ix(\tau-t)}=\frac{1}{2\pi}\int_{-\infty}^{+\infty}d\tau E(\tau)e^{-y(\tau-t)}[\int_{-\infty}^{+\infty}dx\ e^{ix(\tau-t)}dx]$$
$$=\int_{-\infty}^{+\infty}d\tau\,E(\tau)e^{-y(\tau-t)}\delta(\tau-t)=E(t)$$

In addition, since $E(t)$ is real $\Rightarrow$ $[E(\omega)]^*=E(-\omega^*)$.

2.2.2 Linear Optical Susceptibility

Note that

$$P^{(1)}(t) = \int_{-\infty}^{+\infty} R^{(1)}(t-\tau)E(\tau)d\tau$$

$$= \int_{-\infty}^{+\infty} R^{(1)}(\tau')E(t-\tau')d\tau'$$

$$= \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} d\tau' R^{(1)}(\tau')E(\omega)e^{-i\omega(t-\tau')},$$

$$= \int_{-\infty}^{+\infty} d\omega\, \chi^{(1)}(-\omega_\sigma;\omega)E(\omega)e^{-i\omega t}$$

where $\chi^{(1)}(-\omega_\sigma;\omega) \equiv \int_{-\infty}^{+\infty} d\tau R^{(1)}(\tau)e^{i\omega\tau}$ (8)

and $\omega_\sigma = \omega$.

- **Causality Condition in the Frequency Domain:** $R^{(1)}(\tau) = 0$ when $\tau < 0$ [in time domain]. $e^{i\omega\tau} \to 0$ when $\tau \to +\infty$ if ω in the upper half-plane. Thus, Eq. (8) converges if ω is in the upper half-plane, *i.e.*,

$\chi^{(1)}(-\omega;\omega)$ **is analytic in the upper half-plane of ω.**

- **Reality Condition in the Frequency Domain:** $R^{(1)}(\tau)$ is a real function of τ in the time domain $\Leftrightarrow$ $[\chi^{(1)}(-\omega;\omega)]^* = \chi^{(1)}(\omega^*;-\omega^*)$.

2.2.3 Second-Order Nonlinear Optical Susceptibility

By expressing $E(t)$ in the frequency domain:

$$P^{(2)}(t) = \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2 R^{(2)}(\tau_1,\tau_2)E(t-\tau_1)E(t-\tau_2)$$

$$= \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2 R^{(2)}(\tau_1,\tau_2)E(\omega_1)E(\omega_2)e^{-i\{\omega_1(t-\tau_1)+\omega_2(t-\tau_2)\}}.$$

Let $\omega_\sigma = \omega_1 + \omega_2$,

$$P^{(2)}(t) = \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2 \chi^{(2)}(-\omega_\sigma;\omega_1,\omega_2)E(\omega_1)E(\omega_2)e^{-i\omega_\sigma t}. \quad (9)$$

Here

$$\chi^{(2)}(-\omega_\sigma;\omega_1,\omega_2) \equiv \int_{-\infty}^{+\infty} d\tau_1 \int_{-\infty}^{+\infty} d\tau_2 R^{(2)}(\tau_1,\tau_2)e^{i(\omega_1\tau_1+\omega_2\tau_2)}$$

- **Causality Condition in the Frequency Domain:**

$\chi^{(2)}(-\omega_\sigma;\omega_1,\omega_2)$ **is analytic when both ω_1 and ω_2 lie in the upper half-plane.**

- **Reality Condition:** $[\chi^{(2)}(-\omega_\sigma;\omega_1,\omega_2)]^* = \chi^{(2)}(\omega_\sigma{}^*;-\omega_1{}^*,-\omega_2{}^*)$.

- **Intrinsic Permutation Symmetry:** $\chi^{(2)}{}_{\mu\alpha\beta}(-\omega_\sigma;\omega_1,\omega_2) = \chi^{(2)}{}_{\mu\beta\alpha}(-\omega_\sigma;\omega_2,\omega_1)$.

2.2.4 N*th*-Order Nonlinear Optical Susceptibility

Let $\omega_\sigma = \omega_1 + \cdots + \omega_n$,

$$P^{(n)}(t) = \int_{-\infty}^{+\infty} d\omega_1 \cdots \int_{-\infty}^{+\infty} d\omega_n \chi^{(n)}(-\omega_\sigma;\omega_1,\cdots,\omega_n) E(\omega_1)\cdots E(\omega_n) e^{-i\omega_\sigma t} \tag{10}$$

Here

$$\chi^{(n)}(-\omega_\sigma;\omega_1,\cdots,\omega_n) \equiv \int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_n R^{(n)}(\tau_1,\cdots,\tau_n) e^{i\sum_j \omega_j \tau_j}$$ and

$$P^{(n)}(\omega_\sigma) = \chi^{(n)}(-\omega_\sigma;\omega_1,\cdots,\omega_n) | E(\omega_1)\cdots E(\omega_n)$$

- **Causality Condition in the Frequency Domain:**

$\chi^{(n)}(-\omega_\sigma;\omega_1,\cdots,\omega_n)$ **is analytic when all the frequencies** $\omega_1,\cdots,\omega_n$ **lie in the upper half-plane.**

- **Reality Condition:** $[\chi^{(n)}(-\omega_\sigma;\omega_1,\cdots,\omega_n)]^* = \chi^{(n)}(\omega_\sigma{}^*;-\omega_1{}^*,\cdots,-\omega_n{}^*)$.

- **Intrinsic Permutation Symmetry:** $\chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)$ is invariant under all ***n*!** permutations of the n pairs ($\alpha_1\omega_1$), …., ($\alpha_n\omega_n$).

2.3 Symmetry Properties of the Susceptibility Tensors

2.3.1 Permutation Symmetry

- **Intrinsic Permutation Symmetry of** $\chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)$ **:** $\chi^{(n)}$ is invariant under all ***n*!** permutations of the ***n*** pairs ($\alpha_1\omega_1$), …., ($\alpha_n\omega_n$).

Intrinsic permutation symmetry is a fundamental property of the nonlinear susceptibilities which arises from the principles of time-invariance and causality and which applies universally.

- **Overall Permutation Symmetry of** $\chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)$ **:** $\chi^{(n)}$ is invariant under all ***n*!** permutations of the ***n*** pairs ($\alpha_1\omega_1$), …., ($\alpha_n\omega_n$) and the additional pair ($\mu, -\omega_\sigma$), i.e., The $(\boldsymbol{n}+\mathbf{1})!$ permutations of the pairs $(\alpha_1\omega_1)$, …., $(\alpha_n\omega_n)$ and $(\mu, -\omega_\sigma)$ leave $\chi^{(n)}$ unchange. Note that this symmetry is an approximation which is valid *when all of the optical frequencies are far separated from the transition frequencies of the nonlinear optical medium* (*i.e.*, medium is transparent at all the relevant frequencies).

2.3.2 Time-Reversal Symmetry of $\chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)$

If the Hamiltonian of a dynamical system is invariant under time-reversal, then the dynamical system shall possess time-reversal symmetry.

What is the time-reversal operation for a dynamical system?

Recall there are two types of dynamical variables under time-reversal operation $t \to -t$. For example, in Classical Mechanics (CM) we can find the following two types of dynamical variable:

(1) invariant under time-reversal

such as $\vec{r} \to \vec{r} \quad when\ t \to -t$, and $f(\vec{r}) \to f(\vec{r}) \quad when\ t \to -t$;

$g(p^2 = \vec{p}\cdot\vec{p}) \to g(p^2) \quad when\ t \to -t$.

(2) change sign under time-reversal

$$\vec{p} \equiv m\frac{d\,\vec{r}}{d\,t} \xrightarrow{t\to -t} -\vec{p}.$$

In Quantum Mechanics (QM), we have

(1) invariant under time-reversal

which in fact are all real operators such as $\vec{r} \to \vec{r}$, $g(p^2 = \vec{p}\cdot\vec{p}) \to g(p^2)$ (e.g., kinetic energy), $f(\vec{r}) \to f(\vec{r})$ (potential energy) when taking time-reversal operation (*i.e.*, complex conjugate).

(2) change sign under time-reversal

which are all pure imaginary operators such as

$\vec{p} = -i\hbar\nabla \to -\vec{p}$.

Therefore, the time-reversal operation can be described by

I. Classical Mechanics (CM)	II. Quantum Mechanics (QM)
$t \to -t$	$O \to O^*$

When Hamiltonian H_0 consists of a sum of kinetic energy term $g(p^2)$, and an interaction potential energy which is a real function of the vector coordinates

$\vec{r}_j$ **and** $\vec{R}_k$, then

- H_0 is invariant under time-reversal (CM);
- H_0 is a **real operator** (QM).

Considering that $H_0 u_i(\Theta) = E_i u_i(\Theta)$,

(1) both H_0 **and** E_i are real. Note that $u_i(\Theta)$ [the energy eigenfunctions] can be chosen to be real by properly choosing a phase reference; and therefore

(2) dipole-moment element is real too. This can be seen from

$e[r^\alpha]_{ab} = \int d\Theta\, u_a{}^*(\Theta) e r^\alpha u_b(\Theta) \quad \to e[r^\alpha]_{ab}$, which is a real quantity!

(3) from

$$\chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n) = \frac{Ne^{n+1}}{n!\hbar^n} S_r \sum_{ab_1\cdots b_n} \rho_0(a) \frac{[r^\mu]_{ab_1}[r^{\alpha_1}]_{b_1b_2}\cdots[r^{\alpha_n}]_{b_na}}{(\Omega_{b_1a}-\omega_1\cdots-\omega_n)(\Omega_{b_2a}-\omega_2\cdots-\omega_n)\cdots(\Omega_{b_na}-\omega_n)}$$

Note $\rho_0(a) \sim e^{-E_a/k_BT}$ is real and $\Omega_{b_1a} \equiv \text{real}$.

By exploiting time reversal operation,

(I) $[\chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)]^* = \chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma{}^*;\omega_1{}^*,\cdots,\omega_n{}^*)$, *i.e.*,

if $(-\omega_\sigma;\omega_1,\cdots,\omega_n)$ are real, then

$[\chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)]^* = \chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)$.

(II) From Reality condition

$$\begin{aligned}[\chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)]^* &\Rightarrow (\textit{reality condition}) \\ &= \chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(\omega_\sigma{}^*;-\omega_1{}^*,\cdots,-\omega_n{}^*)\end{aligned}.$$

From (I) and (II), $\chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(\omega_\sigma;-\omega_1,\cdots,-\omega_n) = \chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)$,

i.e., if $\chi^{(n)}$ is invariant under time-reversal operation, then $\chi^{(n)}$ is unchanged when all the frequencies $(\omega_\sigma;\omega_1,\cdots,\omega_n)$ of $\chi^{(n)}$ are negated.

A simple conclusion from this result: by considering the linear optics with n=1,

$$\begin{aligned}\chi^{(1)}{}_{\mu\alpha}(-\omega;\omega) &= \chi^{(1)}{}_{\mu\alpha}(\omega;-\omega) \quad \textbf{[time-reversal invariant]} \\ &= \chi^{(1)}{}_{\alpha\mu}(-\omega;\omega) \quad \textbf{[overall permutation symmetry]}\end{aligned}.$$

Therefore,

$\chi^{(1)}{}_{\mu\alpha}(-\omega;\omega)=\chi^{(1)}{}_{\alpha\mu}(-\omega;\omega)$ is a symmetric tensor. Therefore, we can diagonalize it in an appropriate coordinates system. This is the basis of the well-known Reciprocity Theorem in Optics. However, like the overall permutation symmetry, time-reversal invariance breaks down when any of the optical frequencies near a transition frequency of the medium, where damping effect becomes important.

2.3.3 Spatial Symmetry of $\chi^{(n)}{}_{\mu\alpha_1\alpha_2\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)$

Neumann's Principle, which is applicable to all of the physical properties of a system that exhibits spatial symmetry, states

Any physical property (*i.e.*, the dynamical variables) must be invariant under any transformation of coordinates that is governed by a valid symmetry operation for the medium (*i.e.*, belong to the symmetry group of the system)

To illustrate the principle, let us first consider $\vec{x}\,'=\overleftrightarrow{R}\vec{x}$ with $\overleftrightarrow{R}$ denoting a rotation, which can be either proper or improper operation. From the length invariant property,

$(\vec{x}\,')^T(\vec{x}\,')=(\vec{x})^T(\vec{x}) \quad\Rightarrow\quad \overleftrightarrow{R}^{-1}=\overleftrightarrow{R}^T$.

Hence $x'_\alpha=R_{\alpha i}x_i \quad\Rightarrow\quad x_i=(R^{-1})_{i\alpha}x'_\alpha=R_{\alpha i}x'_\alpha$.

Similarly, for other polar vectors such as $P'_\mu(t)=R_{\mu i}P_i(t),\quad E'_\mu=R_{\mu i}E_i$.

Let us examine the optical response in two different coordinate systems.

$$P^{(1)}{}_\mu(t)=\int_{-\infty}^{+\infty}\chi^{(1)}_{\mu\alpha}(-\omega;\omega)E_\alpha(\omega)e^{-i\omega t}d\omega \quad \text{[old]}$$
$$P^{(1)}{}'_\mu(t)=\int_{-\infty}^{+\infty}\chi^{(1)}_{\mu\alpha}{}'(-\omega;\omega)E'_\alpha(\omega)e^{-i\omega t}d\omega \quad \text{[new]}$$

We can deduce the transformation rule for 2nd rank tensor,

$$[\chi^{(1)}{}'(\text{new})]_{\mu\alpha}=R_{\mu i}R_{\alpha j}[\chi^{(1)}(\text{old})]_{ij}\equiv[R\chi^{(1)}(\text{old})R^T]_{\mu\alpha}.$$

Similar result for higher rank susceptibility tensor can also be obtained.

Neumann's Principle requires **the elements of a susceptibility tensor taken with respect to two coordinate systems, which are related by one of the symmetry operations of the medium, must be identical.** This leads to a simultaneous equation system of the susceptibility tensor components.

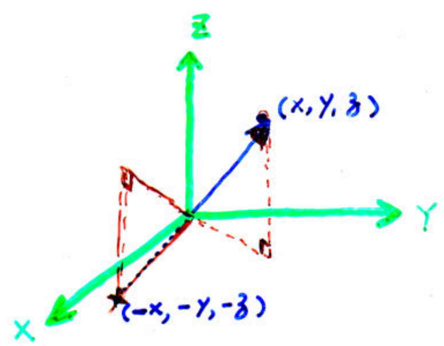
$$\chi^{(n)\prime}{}_{\mu\alpha_1\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n)=\chi^{(n)}{}_{\mu\alpha_1\cdots\alpha_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n) \quad \textbf{[Neumann's Principle]}$$

$$=R_{\mu u}R_{\alpha_1 a_1}\cdots R_{\alpha_n a_n}\chi^{(n)}{}_{u a_1\cdots a_n}(-\omega_\sigma;\omega_1,\cdots,\omega_n) \quad \textbf{[Transformation of a Tensor]}$$

We therefore can use Neumann's Principle to reduce the number of the susceptibility tensor elements. The above equations impose restrictions on the elements of the susceptibility tensors. For example, let us consider the case of

(1) $\chi^{(n)}{}_{\mu\alpha_1\cdots\alpha_n}$ of a medium with an inversion symmetry. The inversion operation is

described by $R_{\alpha\beta}=-\delta_{\alpha\beta}$.



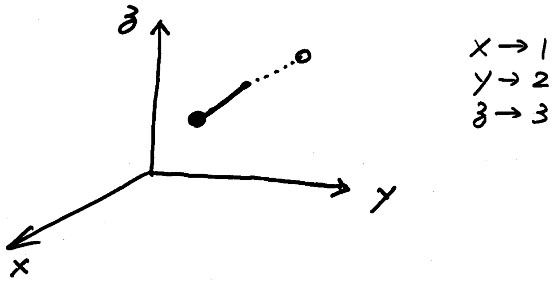
$\chi^{(n)\prime}{}_{\mu\alpha_1\cdots\alpha_n}=R_{\mu u}R_{\alpha_1 a_1}\cdots R_{\alpha_n a_n}\chi^{(n)}{}_{u a_1\cdots a_n}=(-1)^{n+1}\chi^{(n)}{}_{\mu\alpha_1\cdots\alpha_n}$ implies $\chi^{(n)}{}_{\mu\alpha_1\cdots\alpha_n}$ vanishes when n is even for a medium with an inversion symmetry.

(2) $\chi^{(3)}{}_{\mu\alpha_1\alpha_2\alpha_3}$ of an isotropic medium

An isotropic medium is a material which is invariant under (i) any rotation (proper); (ii) any reflection (improper), and (iii) inversion.
The invariant condition for any reflection can be reduced to be invariant with reflections in three mutually orthogonal planes.

Let us first consider

- reflection in the yz-plane: $\mathbf{1}(x)\rightarrow-\mathbf{1} \quad \mathbf{2}(y)\rightarrow\mathbf{2} \quad \mathbf{3}(z)\rightarrow\mathbf{3}$



$\Rightarrow \chi^{(3)}$ with an odd number of x indices must be vanish.

- reflection in the xz, and xy planes $\Rightarrow \chi^{(3)}$ with an odd number of *y* (and *z*) indices must vanish.

$$\Rightarrow \begin{array}{l} \chi^{(3)}{}_{iiii}: \chi^{(3)}{}_{1111}, \chi^{(3)}{}_{2222}, \chi^{(3)}{}_{3333}; \\ \chi^{(3)}{}_{iijj}: \chi^{(3)}{}_{1122}, \chi^{(3)}{}_{1133}, \chi^{(3)}{}_{2233}, \ etc.; \\ \chi^{(3)}{}_{ijij}: \chi^{(3)}{}_{1212}, \chi^{(3)}{}_{1313}, \chi^{(3)}{}_{2323}, \ etc.; \\ \chi^{(3)}{}_{ijji}: \chi^{(3)}{}_{1221}, \chi^{(3)}{}_{1331}, \chi^{(3)}{}_{2332}, \ etc.; \end{array}$$

Now let us further consider

- 90° rotation about z-axis: $\mathbf{1 \to 2, \quad 2 \to -1, \quad 3 \to 3}$

$$\Rightarrow \begin{array}{l} \chi^{(3)}{}_{iiii}: \chi^{(3)}{}_{1111} = \chi^{(3)}{}_{2222}; \\ \chi^{(3)}{}_{iijj}: \chi^{(3)}{}_{1122} = \chi^{(3)}{}_{2211}, \chi^{(3)}{}_{1133} = \chi^{(3)}{}_{2233}; \\ \chi^{(3)}{}_{ijij}: \chi^{(3)}{}_{1212} = \chi^{(3)}{}_{2121}; \\ \chi^{(3)}{}_{ijji}: \chi^{(3)}{}_{1221} = \chi^{(3)}{}_{2112}; \end{array}$$

- 90° rotation about x-axis: $\mathbf{1 \to 1 \quad 2 \to 3 \quad 3 \to -2}$

  y-axis: $\mathbf{1 \to -3 \quad 2 \to 2 \quad 3 \to 1}$

$$\Rightarrow \begin{array}{l} \chi^{(3)}{}_{iiii}: \chi^{(3)}{}_{1111} = \chi^{(3)}{}_{2222} = \chi^{(3)}{}_{3333}; \\ \chi^{(3)}{}_{iijj}: \chi^{(3)}{}_{1133} = \chi^{(3)}{}_{3311} = \chi^{(3)}{}_{1122} = \chi^{(3)}{}_{2211} = \chi^{(3)}{}_{2233} = \chi^{(3)}{}_{3322}; \\ \chi^{(3)}{}_{ijij}: \chi^{(3)}{}_{1212} = \chi^{(3)}{}_{2121} = \chi^{(3)}{}_{3131} = \chi^{(3)}{}_{1313} = \chi^{(3)}{}_{2323} = \chi^{(3)}{}_{3232}; \\ \chi^{(3)}{}_{ijji}: \chi^{(3)}{}_{2332} = \chi^{(3)}{}_{3223} = \chi^{(3)}{}_{3113} = \chi^{(3)}{}_{1331} = \chi^{(3)}{}_{1221} = \chi^{(3)}{}_{2112} \end{array}$$

Let us then exploit the rotation about z-axis by arbitrary angle θ, which is known to have the rotational matrix

$$R = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Thus, after rotation

$$\begin{aligned} \chi^{(3)}{}_{1111}[\text{old}] &= \chi^{(3)}{}_{1111}{}'[\text{new}] \\ &= \sum_i R_{1i}R_{1i}R_{1i}R_{1i}\chi^{(3)}{}_{iiii} + \sum_{ij} R_{1i}R_{1j}R_{1i}R_{1j}\chi^{(3)}{}_{ijij} + \sum_{ij} R_{1i}R_{1i}R_{1j}R_{1j}\chi^{(3)}{}_{iijj} + \sum_{ij} R_{1i}R_{1j}R_{1j}R_{1i}\chi^{(3)}{}_{ijji}. \\ &= (\cos^4\theta + \sin^4\theta)\chi^{(3)}{}_{1111} + 2\cos^2\theta\sin^2\theta(\chi^{(3)}{}_{1212} + \chi^{(3)}{}_{1122} + \chi^{(3)}{}_{1221}) \end{aligned}$$

$$\chi^{(3)}{}_{1111} = \chi^{(3)}{}_{1122} + \chi^{(3)}{}_{1212} + \chi^{(3)}{}_{1221}$$

Finally, by invoking Kleiman symmetry [note this is valid only for nonresonant media]:

$$\chi^{(3)}{}_{1122} = \chi^{(3)}{}_{1212} = \chi^{(3)}{}_{1221} \quad \Rightarrow \quad \chi^{(3)}{}_{1122} = \frac{1}{3}\chi^{(3)}{}_{1111},$$

i.e., only one independent component $\chi^{(3)}{}_{1111}$ left to be measured.

2.4 Resonant Nonlinear Susceptibility Tensor

Consider an applied optical field that comprise a superposition of quasi-monochromatic waves

$$E(t)=\frac{1}{2}\sum_{\omega}[E_{\omega}(t)e^{-i\omega t}+c.c.].$$

The polarization induced in the medium can be expressed as

$$P(t)=\frac{1}{2}\sum_{\omega}[P_{\omega}(t)e^{-i\omega t}+c.c.].$$

Here the quasi-monochromatic spectral component $E_{\Omega}(t)=\int_{-\infty}^{+\infty}E_{\Omega}(\omega-\Omega)e^{-i(\omega-\Omega)t}d\omega$ denotes an optical field with its spectrum centered at Ω.

Recall

$$P(t)=\int_{-\infty}^{+\infty}\chi^{(1)}(-\omega;\omega)E_{\omega}(t)e^{-i\omega t}d\omega,$$

we then achieve $P_{\Omega}(t)=\int_{-\infty}^{+\infty}\chi^{(1)}(-\omega;\omega)E_{\Omega}(\omega-\Omega)e^{-i(\omega-\Omega)t}d\omega$.

2.4.1 Adiabatic Response

When Ω is far below the transition frequencies of the medium, $\Omega\ll\omega_{ng}$,

$\chi^{(1)}(-\omega;\omega)$ is a slowly-varying function of frequency ω around Ω.

Thus, we can express it in Taylor's series at Ω

$$\begin{aligned}P_{\Omega}(t)&=\int_{-\infty}^{+\infty}\chi^{(1)}(-\omega;\omega)E_{\Omega}(\omega-\Omega)e^{-i(\omega-\Omega)t}d\omega\\&=\int_{-\infty}^{+\infty}[\chi^{(1)}(-\Omega;\Omega)+\frac{d\chi^{(1)}(-\omega;\omega)}{d\omega}|_{\Omega}\cdot(\omega-\Omega)+\cdots]E_{\Omega}(\omega-\Omega)e^{-i(\omega-\Omega)t}d\omega\end{aligned}.$$

Then,

$$P_{\Omega}(t)\simeq\{\chi^{(1)}(-\Omega;\Omega)E_{\Omega}(t)+i\frac{d\chi^{(1)}(-\omega;\omega)}{d\omega}|_{\Omega}\cdot\frac{dE_{\Omega}(t)}{dt}\}\ .$$

For an adiabatically applied field, the magnitude of the second term must be much smaller than the first term, which leads to

$$\|\frac{1}{\chi^{(1)}(-\Omega;\Omega)}\cdot\frac{d\chi^{(1)}(-\omega;\omega)}{d\omega}|_{\Omega}\cdot\frac{1}{E_{\Omega}(t)}\frac{dE_{\Omega}(t)}{dt}\|\ll 1\ . \qquad \text{(I)}$$

Recall that

$$\chi^{(1)}(-\omega;\omega)=\frac{Ne^2}{\hbar}\sum_b |\hat{e}_\omega\cdot\vec{r}_{ab}|^2\{\frac{1}{(\omega_{ba}-\Omega-i\Gamma)^2}-\frac{1}{(\omega_{ba}+\Omega+i\Gamma)^2}\}.$$

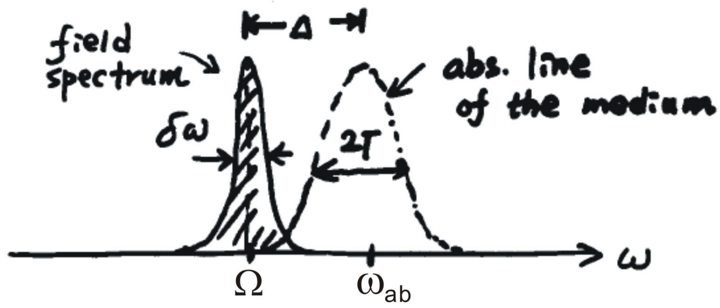
Near a resonance $\Delta\equiv\omega_{ba}-\Omega\ll\omega_{ba}+\Omega$, therefore the inequality (I) becomes

$$\|\frac{1}{\Delta-i\Gamma}\cdot\frac{1}{E_\Omega(t)}\frac{dE_\Omega(t)}{dt}\|\ll 1\quad. \qquad \text{(II)}$$

From the characteristic rate of change of the field envelope:

$|\frac{E_\Omega(t)}{\tau_c}|\sim|\frac{dE_\Omega(t)}{dt}|$ with $\tau_c\sim\frac{1}{\delta\omega}\equiv$ field correlation time.

Inequality (II) then can be reduced to $|\frac{\Delta-i\Gamma}{\delta\omega}|\gg 1$ (III)



Inequality (III) implies that for the adiabatic response to be valid, *the frequency spread of the pulse should not overlap the medium's transition frequency*, implying that *the field correlation time* τ_c *must be longer than the impulse response time of the polarization*

$\tau_c\gg|\frac{1}{\Delta-i\Gamma}|$.

2.4.2 Adiabatic Condition Violated

When Ω is tuned closed to resonance with a transition and the fields are quasi-monochromatic.

Note $\chi^{(1)}(-\omega;\omega)=\int_{-\infty}^{+\infty}R^{(1)}(\tau)e^{i\omega\tau}d\tau$.

By defining an envelope response function by $\phi(\tau)=R^{(1)}(\tau)e^{i\omega\tau}$, we found

$$\chi^{(1)}(-\omega;\omega)=\int_{-\infty}^{+\infty}\phi(\tau)d\tau=\frac{Ne^2}{\hbar}\frac{|\hat{e}_\omega\cdot r_{ba}|^2}{\omega_0{}^2-\omega^2-i\Gamma\omega}$$

$$\rightarrow\quad \phi(\tau)=\begin{cases}\frac{iNe^2}{\hbar}|\hat{e}_\omega\cdot r_{ba}|^2\,e^{-(i\Delta+\Gamma)\tau} & \tau\ge 0\\ 0 & \tau<0\end{cases}$$

$P^{(1)}(t)=\int_{-\infty}^{+\infty}\phi(t-\tau)E(\tau)d\tau=\frac{iNe^2}{\hbar}|\hat{e}_\omega\cdot\vec{r}_{ab}|^2\int_{-\infty}^{t}E(\tau)e^{-(i\Delta+\Gamma)(t-\tau)}d\tau$ is the polarization envelope. By using integration by part,

$$P^{(1)}(t)=\frac{iNe^2}{\hbar}|\hat{e}_\omega\cdot\vec{r}_{ab}|^2\cdot\left[\int_{-\infty}^{t}E(\tau)d\tau+(i\Delta+\Gamma)\int_{-\infty}^{t}d\tau\int_{-\infty}^{\tau}d\tau' E(\tau)+\cdots\right].$$

The expansion is a good approximation if $|\Delta-i\Gamma|\tau_c\ll 1$ for a coherent transient regime.

When $E(t)$ acting on the medium consists of a short pulse, incident at time $t\sim 0$, whose duration τ_p is very much less than the polarization dephasing time $\tau_p\ll|\Delta-i\Gamma|^{-1}$,

$P^{(1)}(t)=\frac{iNe^2}{\hbar}|\hat{e}_\omega\cdot\vec{r}_{ab}|^2 E_1(0)\tau_p e^{-(i\Delta+\Gamma)t}=\chi_{equ}^{(1)}E_1(0)$, *i.e.*,

for pulsed excitation in the coherent transient regime, the response of the medium depends on the **field area** [$E_1(0)\tau_p$], rather than the instantaneous field. In this case, an equivalent susceptibility can be defined to be

$\chi_{equ}^{(1)}(-\omega_1;\omega_1)=\chi^{(1)}(-\omega_1;\omega_1)\cdot\tau_p\cdot(i\Delta+\Gamma)$, implying that in the transient regime, it is still possible to write an expression for the polarization in the familiar form of the adiabatic response, except that the true susceptibility is reduced by τ_p/T_2.

2.5 Spatial Dispersion of Nonlinear Susceptibility Tensor

In the previous discussion on the optical response function, we have used a local response assumption, which states

Polarization at a point in the medium is assumed to be determined completely by the electric field at that point.

Now note that the polarization can be determined by the electric field in the neighborhood of that point, the time-invariance used in the previous discussion should then be argumented by a corresponding principle of **Spatial-Invariance**.

$$P^{(n)}(\vec{r},t)=\int_{-\infty}^{+\infty}d\tau_1\cdots\int_{-\infty}^{+\infty}d\tau_n\int_{-\infty}^{+\infty}d\vec{r}_1\cdots\int_{-\infty}^{+\infty}d\vec{r}_n\,R^{(n)}(\vec{r}_1\tau_1,\vec{r}_2\tau_2\cdots,\vec{r}_n\tau_n)|E(\vec{r}_1,t-\tau_1)E(\vec{r}_2,t-\tau_2)\cdots E(\vec{r}_n,t-\tau_n),$$

and then

- Intrinsic Permutation Symmetry requires $(\alpha_1\tau_1\vec{r}_1),\ldots,(\alpha_n\tau_n\vec{r}_n)$ can be exchanged without affecting $R^{(n)}$.
- By using $E(\vec{r},t)\equiv\int_{-\infty}^{+\infty}d\omega\int_{-\infty}^{+\infty}d\vec{k}\,E(\vec{k},\omega)e^{i\vec{k}\cdot\vec{r}-i\omega t}$, $\chi^{(n)}$ will depend on $\vec{k}$ as well as

ω [*i.e.*, Spatial dispersion ($\vec{k}$ -dependent) + temporal dispersion have been included].

$$P^{(n)}(\vec{r},t) =$$

$$\int_{-\infty}^{+\infty} d\omega_1 \cdots \int_{-\infty}^{+\infty} d\omega_n \int_{-\infty}^{+\infty} d\vec{k}_1 \cdots \int_{-\infty}^{+\infty} d\vec{k}_n\ \chi^{(n)}(-\omega_\sigma, -\vec{k}_p; \vec{k}_1\omega_1, \cdots, \vec{k}_n\omega_n) | E(\vec{k}_1\omega_1) \cdots E(\vec{k}_n\omega_n) e^{i(\omega_\sigma t - \vec{k}_p \cdot \vec{r})}$$

where

$$\chi^{(n)}(-\omega_\sigma, -\vec{k}_p; \vec{k}_1\omega_1, \cdots, \vec{k}_n\omega_n) =$$

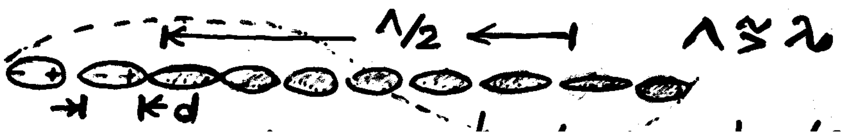
$$\int_{-\infty}^{+\infty} d\tau_1 \cdots \int_{-\infty}^{+\infty} d\tau_n \int_{-\infty}^{+\infty} d\vec{r}_1 \cdots \int_{-\infty}^{+\infty} d\vec{r}_n\ R^{(n)}(\vec{r}_1\tau_1, \cdots, \vec{r}_n\tau_n) e^{i\sum_j (\omega_j\tau_j - \vec{k}_j \cdot \vec{r}_j)}$$

with

$\omega_\sigma = \sum_{j=1}^{n} (\pm\omega_j)$; $\vec{k}_p = \sum_{j=1}^{n} (\pm\vec{k}_j)$ involve $(\alpha_1\omega_1\vec{k}_1), \ldots, (\alpha_n\omega_n\vec{k}_n)$ permutation symmetry.

Spatial dispersion is important when

- Polarizable units are strongly coupled such as cooperative effect like polariton shown below



Electric-dipole approximation which neglects $\vec{k}$ -dependence of $\chi^{(n)}(-\omega_\sigma, -\vec{k}_p; \vec{k}_1\omega_1, \cdots, \vec{k}_n\omega_n)$ implies **local field is uniform when** $\lambda \gg d$ where d is the scale length of polarizable units.