Nonlinear response function

To account for the nonlinear response of the polarization density $\boldsymbol{P}$ under an applied electric field $\boldsymbol{E}$ we perform a Taylor expansion with $\boldsymbol{P}(\boldsymbol{E}) = \boldsymbol{P}^{(1)}(\boldsymbol{E}) + \boldsymbol{P}^{(2)}(\boldsymbol{E}) + \ldots$. Here, $\boldsymbol{P}^{(n)}(\boldsymbol{E})$ is proportional to a product of n electric field components. The first order term was treated in Lecture 02; the second order term has the general expression below for a **local, homogeneous and time-translation invariant** medium:

$$P_i^{(2)}(t) = \epsilon_0 \int d\tau_1 \int d\tau_2 \, R_{ijk}^{(2)}(\tau_1, \tau_2) E_j(t - \tau_1) E_k(t - \tau_2) \tag{1}$$

where the subscripts i, j, k take values among 3 orthogonal direction x, y, z along the principal axes. We substitute each real field by its Fourier decomposition $E_i(t) = \int d\omega \, E_i(\omega) e^{-i\omega t}$:

$$\begin{aligned} P_i^{(2)}(t) &= \varepsilon_0 \int d\omega_1 \int d\omega_2 \int d\tau_1 \int d\tau_2 \, R_{ijk}^{(2)}(\tau_1, \tau_2) \\ &\quad E_j(\omega_1) E_k(\omega_2) \exp\left[-i \left\{\omega_1 \left(t - \tau_1\right) + \omega_2 \left(t - \tau_2\right)\right\}\right] \qquad (2) \\ &= \varepsilon_0 \iint d\omega_1 d\omega_2 \left(\iint d\tau_1 d\tau_2 \, R_{ijk}^{(2)}(\tau_1, \tau_2) e^{i\omega_1\tau_1 + i\omega_2\tau_2} \right) \\ &\quad E_j(\omega_1) E_k(\omega_2) e^{-i(\omega_1 + \omega_2)t} \qquad (3) \end{aligned}$$

Nonlinear response susceptibility

In the last expression, we can identify the term in parenthesis with the second-order (quadratic) nonlinear susceptibility

$$\chi^{(2)}_{ijk}(-\omega_\sigma : \omega_1, \omega_2) = \iint d\tau_1 d\tau_2 \, R^{(2)}_{ijk}(\tau_1, \tau_2) e^{i\omega_1\tau_1 + i\omega_2\tau_2} \tag{4}$$

which is the two-dimensional Fourier transform of the second-order polarization response function. We introduced a short-hand notation:

$$\omega_\sigma = \omega_1 + \omega_2 = \sum_\alpha \omega_\alpha$$

that will become useful when discussing permutation symmetries.
Taking the Fourier Transform $\frac{1}{2\pi}\int dt\, \boldsymbol{P}^{(2)}(t)e^{i\omega t}$ of eq. (3) and using the identity $\frac{1}{2\pi}\int dt\, e^{i(\omega-\omega_\sigma)t} = \delta(\omega - \omega_\sigma)$ we find the expression for each complex frequency component of the polarization density:

$$P^{(2)}_i(\omega) = \varepsilon_0 \iint d\omega_1 d\omega_2 \, \chi^{(2)}_{ijk}(-\omega_\sigma; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2) \delta(\omega - \omega_\sigma) \tag{5}$$

Intrinsic permutation symmetry

We can swap the pairs of variables (ω_1, j) and (ω_2, k) in the mathematical expressions above without changing their physical meaning; the nonlinear susceptibility must, therefore, satisfy the so-called **intrinsic permutation symmetry**:

$$\chi^{(2)}_{ijk}(-\omega_\sigma; \omega_1, \omega_2) = \chi^{(2)}_{ikj}(-\omega_\sigma; \omega_2, \omega_1)$$

Moreover, if losses can be neglected, the $\chi^{(2)}$ tensor remains invariant upon any permutations of $(-\omega_\sigma, i)$, (ω_1, j) and (ω_2, k) (**full permutation symmetry**) for example

$$\chi^{(2)}_{ijk}(-\omega_\sigma; \omega_1, \omega_2) = \chi^{(2)}_{jik}(\omega_1; -\omega_\sigma, \omega_2) = \chi^{(2)*}_{jik}(-\omega_1; \omega_1 + \omega_2, -\omega_2)$$

The leftmost susceptibility corresponds to sum-frequency generation between ω_1 and ω_2 while the rightmost corresponds to difference frequency generation between $\omega_1 + \omega_2$ and ω_2

Generalization to $\boldsymbol{P}^{(n)}$

If we introduce the notation $\vec{\omega} = (\omega_1, ..., \omega_n)$ we have

$$P_\beta^{(n)}(\omega) = \varepsilon_0 \int d\vec{\omega}\, \chi^{(n)}_{\beta\alpha_1\ldots\alpha_n}(-\omega_\sigma; \vec{\omega}) E_{\alpha_1}(\omega_1) \ldots E_{\alpha_n}(\omega_n)\delta(\omega - \omega_\sigma)$$

The fact that $\boldsymbol{P}^{(n)}(t)$ is real implies that complex conjugate of the susceptibility satisfies

$$\left[\chi^{(n)}_{\beta\alpha_1\ldots\alpha_n}(-\omega_\sigma; \vec{\omega})\right]^* = \chi^{(n)}_{\beta\alpha_1\ldots\alpha_n}(\omega_\sigma; -\vec{\omega})$$

The right-hand term can be generalized to $\chi^{(n)}_{\beta\alpha_1\ldots\alpha_n}(\omega_\sigma^*; -\vec{\omega}^*)$ for complex frequencies used to model losses under near-resonant conditions.

Often, the exciting field can be approximated by a finite set of monochromatic waves $\boldsymbol{E}(t) = \frac{1}{2}\sum_k \boldsymbol{E}(\omega_k)e^{-i\omega_k t} + c.c.$ whose Fourier components are

$$\boldsymbol{E}(\omega) = \sum_k \left(\frac{1}{2}\boldsymbol{E}(\omega_k)\delta(\omega - \omega_k) + \frac{1}{2}\boldsymbol{E}(\omega_k)^*\delta(\omega + \omega_k)\right)$$

General expression under multiple monochromatic pumps

It can be shown[1] that the frequency components of the resulting n^{th}-order polarization are

$$P_{\beta}^{(n)}(\omega_\sigma) = K(-\omega_\sigma;\vec{\omega})\,\chi^{(n)}_{\beta\alpha_1\ldots\alpha_n}(-\omega_\sigma;\vec{\omega})E_{\alpha_1}(\omega_1)\ldots E_{\alpha_n}(\omega_n) \tag{6}$$

where $K(-\omega_\sigma;\vec{\omega}) = 2^{n+\delta-m}p$ is the **degeneracy factor** for a specific process:

- n is the order of the nonlinear process
- $\delta = 1$ in general, except for optical rectification ($\omega_\sigma = 0$) where $\delta = 0$
- m is the number of applied d.c. ($\omega_\alpha = 0$) fields
- p is the number of *distinguishable* permutation of $\vec{\omega}$

Example: Compute K and verify this expression for second-harmonic generation, sum-frequency generation, and difference frequency generation.

[1] cf. P. Butcher & D. Cotter, *The elements of nonlinear optics*, p. 23

Ex: $\vec{E}(t) = \frac{1}{2}\vec{E}_a e^{-i\omega_a t} + c.c. + \frac{1}{2}\vec{E}_b e^{-i\omega_b t} + c.c.$

$\hookrightarrow \vec{E}(\omega) = \frac{1}{2}\left(\vec{E}_a \delta(\omega-\omega_a) + \vec{E}_a^{\,*} \delta(\omega+\omega_a) + \vec{E}_b\,\delta(\omega-\omega_b) + \vec{E}_b^{\,*}\,\delta(\omega+\omega_b)\right)$

$$\frac{1}{2}P_i^{(2)}(\omega) = \varepsilon_0 \int_{-\infty}^{+\infty} d\omega_1 \int_{-\infty}^{+\infty} d\omega_2\; \chi^{(2)}_{ijk}(-\omega_\sigma:\omega_1,\omega_2)\, \underbrace{E_j(\omega_1)\,E_k(\omega_2)\,\delta(\omega-\omega_\sigma)}$$

$$\left(\frac{1}{2}\right)^2 \left(E_{a,j}\,\delta(\omega_1-\omega_a) + E^*_{a,j}\,\delta(\omega_1+\omega_a) + E_{b,j}\,\delta(\omega_1-\omega_b) + E^*_{b,j}\,(\omega_1+\omega_b)\right)\times$$
$$\left(E_{a,k}\,\delta(\omega_1-\omega_a) + \text{———} \; E^*_{b,k} \text{ —}\right)\delta(\omega-\omega_\sigma)$$

$\hookrightarrow$ sum of 4×4 , 3×3 terms
$(\pm\omega_{a,b})$ (j,k)

* If $\omega_a \neq \omega_b$ $\longrightarrow$ Let's look at the sum frequency $\omega_a+\omega_b$

* $\chi^{(2)}_{ijk}(-\omega_\sigma:\omega_a,\omega_b)\,E_{a,j}\,E_{b,k} + \chi^{(2)}_{\underset{kj}{ijk}}(-\omega_\sigma:\underset{a}{\omega_b},\underset{b}{\omega_a})\,E_{\underset{k}{b,j}}\,E_{\underset{j}{a,k}}$

+ intrinsic perm. sym $(k,\omega_b)\leftrightarrow(j,\omega_a)$

$\frac{1}{2}P_i^{(2)}(\omega_a+\omega_b) = \left(\frac{1}{2}\right)^2\cdot 2\,\chi^{(2)}_{ijk}\left(-(\omega_a+\omega_b):\omega_a,\omega_b\right)E_{a,j}E_{b,k}$ $\rightarrow K=1$ } SFG

Remark : $P_i(-\omega_a-\omega_b) = \chi^{(2)*}_{ijk}\left(-(\omega_a+\omega_b):\omega_a,\omega_b\right)E^*_{a,i}\,E^*_{b,k}$

At the difference frequency $\omega_a-\omega_b$ (if $\omega_a>\omega_b$)

and $P_i^{(2)}(\omega_a-\omega_b) = \chi^{(2)}_{ijk}\left(-(\omega_a-\omega_b):\omega_a\,;\,-\omega_b\right)$ $\rightarrow K=1$

Stimulated emission

$P_i^{(2)}(\omega_b-\omega_a) = P_i^{(2)}(\omega_a-\omega_b)^*$

* Second harmonic generation at $2\omega_a$

$P^{(2)}(2\omega_a) = \frac{1}{2}\,\chi^{(2)}_{ijk}(-2\omega_a:\omega_a,\omega_a)\,E_{a,j}\,E_{a,k}$ $\rightarrow K=\frac{1}{2}$

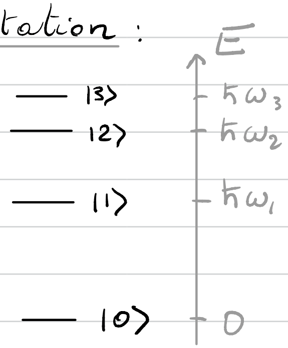
Process	Order n	$-\omega_\sigma;\omega_1,\ldots,\omega_n$	K
Linear absorption/emission and refractive index	1	$-\omega;\omega$	1
Optical rectification (optically-induced d.c. field)	2	$0;\omega,-\omega$	$\frac{1}{2}$
Pockels effect (linear electrooptic effect)	2	$-\omega;0,\omega$	2
Second-harmonic generation	2	$-2\omega;\omega,\omega$	$\frac{1}{2}$
Sum- and difference-frequency mixing, parametric amplification and oscillation	2	$-\omega_3;\omega_1,\pm\omega_2$	1
d.c. Kerr effect (quadratic electrooptic effect)	3	$-\omega;0,0,\omega$	3
d.c.-induced second-harmonic generation	3	$-2\omega;0,\omega,\omega$	$\frac{3}{2}$
Third-harmonic generation	3	$-3\omega;\omega,\omega,\omega$	$\frac{1}{4}$
General four-wave mixing	3	$-\omega_4;\omega_1,\omega_2,\omega_3$	$\frac{3}{2}$
Third-order sum- and difference-frequency mixing	3	$-\omega_3;\pm\omega_1,\omega_2,\omega_2$	$\frac{3}{4}$
Coherent anti-Stokes Raman scattering	3	$-\omega_{AS};\omega_P,\omega_P,-\omega_S$	$\frac{3}{4}$
Optical Kerr effect (optically-induced birefringence), cross-phase modulation, stimulated Raman scattering, stimulated Brillouin scattering	3	$-\omega_S;\omega_P,-\omega_P,\omega_S$	$\frac{3}{2}$
Intensity-dependent refractive index, optical Kerr effect (self-induced and cross-induced birefringence), self-focusing, self-phase and cross-phase modulation, degenerate four-wave mixing	3	$-\omega;\omega,-\omega,\omega$	$\frac{3}{4}$
Two-photon absorption/ionisation /emission	3	$-\omega_1;-\omega_2,\omega_2,\omega_1$ or $-\omega;-\omega,\omega,\omega$	$\frac{3}{2}$ / $\frac{3}{4}$

Butcher & Cotter, p. 26

II) Quantum perturbation theory for $\chi^{(n)}$

1) Multi-level system in thermal equilibrium

Unperturbed Hamiltonian in the energy representation :



$*$ $$\hat{H}_0 = \sum_n \hbar\omega_n \, |n\rangle\langle n|$$

In thermal equilibrium (thermal state)

$$\boxed{\hat{\rho}^{(0)} = \frac{1}{Z} \exp\left(-\beta \hat{H}_0\right)} \quad \text{with} \quad \beta = k_B T$$

and $Z = \mathrm{tr}\left(\exp -\beta\hat{H}_0\right)$

Remark : $\exp -\beta\hat{H}_0 = \sum_k \frac{1}{k!} \left(-\beta\hat{H}_0\right)^k$

but $\left(-\beta\hat{H}_0\right)^k = \left(-\beta \sum_n \hbar\omega_n |n\rangle\langle n|\right)^k = (-\beta)^k \sum_n \left(\hbar\omega_n |n\rangle\langle n|\right)^k$

$$= \sum_n \left(-\beta\hbar\omega_n\right)^k |n\rangle\langle n|$$

so $$\boxed{\hat{\rho}^{(0)} = \frac{1}{Z} \sum_n e^{-\beta\hbar\omega_n} |n\rangle\langle n|} \; ; \quad Z = \sum_n e^{-\beta\hbar\omega_n}$$

For ω_n at optical frequencies , $\hbar\omega_n \gg k_B T$, therefore :

$$\rho^{(0)} \approx |0\rangle\langle 0|$$

↳ Maximally mixed state.

$*$ Time evolution : $i\hbar\dot{\hat{\rho}} = \hat{H}_0\hat{\rho} - \hat{\rho}\hat{H}_0$

↳ Solution $\hat{\rho}(t) = \hat{U}_0(t)\,\hat{\rho}(t=0)\,\hat{U}_0^{+}(t)$ with $\hat{U}_0(t) = e^{-\frac{i\hat{H}_0}{\hbar}t}$

evolution operator

here $\boxed{\hat{U}_0(t) = \sum_n e^{-i\omega_n t} |n\rangle\langle n|}$ → $\hat{\rho}^{(0)}$ is steady state

Remark for a pure state $|\Psi(t)\rangle = \hat{U}_0(t)\,|\Psi_0\rangle$

2) Calculation of $\chi^{(1)}$ for a multilevel system

We apply an external field polarized along $\alpha \in \{x, y, z\}$

$$\vec{E}(t) = E_\alpha \cos\omega t\, \vec{e}_\alpha = \frac{1}{2}\left(E_\alpha e^{-i\omega t} + c.c.\right)\vec{e}_\alpha$$

In the dipole approximation, the light-matter interaction Hamiltonian is : $\hat{H}_c(t) = -\vec{E}\cdot\hat{\vec{\mu}} = -\hat{\mu}_\alpha E_\alpha \cos\omega t$

$$\hat{\vec{\mu}} = \begin{pmatrix} \hat{\mu}_x \\ \hat{\mu}_y \\ \hat{\mu}_z \end{pmatrix} = e \begin{pmatrix} \hat{r}_x \\ \hat{r}_y \\ \hat{r}_z \end{pmatrix}$$ dipole operator.

The solution to $i\hbar\dot{\hat{\rho}} = [\hat{H}_c + \hat{H}_0, \hat{\rho}]$ can be expanded as

$\hat{\rho}(t) = \hat{\rho}^{(0)} + \hat{\rho}^{(1)}(t) + \dots$ where the first order term is

$$\hat{\rho}^{(1)}(t) = \frac{1}{i\hbar}\hat{U}_0(t)\int_{-\infty}^{t} d\tau\, [\hat{H}_c'(t), \hat{\rho}^{(0)}]\, \hat{U}_0^\dagger(t)$$

We defined $\hat{A}'(t) = \hat{U}_0^\dagger(t)\,\hat{A}(t)\,\hat{U}_0(t)$ → interaction picture

Remark : $\langle \hat{A}'(t)\rangle_{\hat{\rho}_0} = tr\left(\hat{\rho}_0 \hat{A}'(t)\right) = tr\left(\hat{\rho}_0 \hat{U}_0^\dagger \hat{A}\hat{U}_0\right)$

$= tr\left(\hat{U}_0(t)\hat{\rho}_0\hat{U}_0^\dagger(t)\,\hat{A}(t)\right) = tr\left(\hat{\rho}(t)\,A(t)\right)$

$= \langle \hat{A}(t)\rangle_{\hat{\rho}(t)}$ → Schrödinger picture

The linear polarization is

$$P^{(1)}_\alpha(t) = \frac{N}{V}\, \mathrm{tr}\left[\hat{\rho}^{(1)}(t)\,\hat{\mu}_\alpha\right] = \varepsilon_0 \int d\omega\, \chi^{(1)}_{\alpha\beta}(\omega) E_\beta(\omega) e^{-i\omega t}$$

Following the steps in Butcher & Cotter (pp. 58-59) we get:

$$\chi^{(1)}_{\alpha\beta}(-\omega_\sigma : \omega) = -\frac{N}{V}\frac{1}{\varepsilon_0 i\hbar}\int_\infty^0 d\tau\, \tilde{R}^{(1)}_{\alpha\beta}(\tau)\, e^{-i\omega\tau}$$

where $\boxed{\tilde{R}^{(1)}_{\alpha\beta}(\tau) = \left\langle \left[\hat{\mu}_\alpha, \hat{\mu}'_\beta(\tau)\right]\right\rangle_{\hat{\rho}^{(0)}}}$

$$= \mathrm{tr}\left\{\hat{\rho}^{(0)}\left[\hat{\mu}_\alpha, \hat{\mu}'_\beta(\tau)\right]\right\}$$

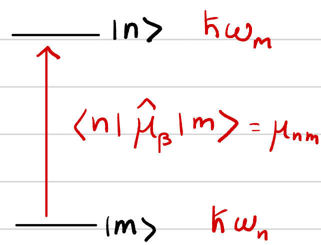
$$\hat{\mu}'_\beta(\tau) = \hat{U}_0^\dagger(\tau)\,\hat{\mu}_\beta\,\hat{U}_0(\tau) = \sum_{nm} e^{+i\omega_m\tau}\,|n\rangle\langle n|\hat{\mu}_\beta|m\rangle\langle m|\, e^{-i\omega_n\tau}$$

$$= \sum_{nm} e^{i\Omega_{nm}}\,\mu^\beta_{nm}\,|n\rangle\langle m|$$

$\Omega_{nm} = -(\omega_n - \omega_m)$

$\mu^\beta_{nm} = \langle n|\hat{\mu}_\beta|m\rangle$

transition dipole



Now, we need to compute the trace, which is a sum of terms of the form:

$$\langle n|\hat{\rho}^{(0)}\hat{A}\hat{B}|n\rangle = \sum_{km}\langle n|\hat{\rho}^{(0)}|k\rangle\langle k|\hat{A}|m\rangle\langle m|\hat{B}|n\rangle$$

$$= \rho^{(0)}_{nn} \sum_m \langle n|\hat{A}|m\rangle\langle m|\hat{B}|n\rangle$$

We get: $\tilde{R}^{(1)}_{\alpha\beta}(\tau) = \sum_n \rho^{(0)}_{nn} \sum_m \Big(\langle n|\hat{\mu}_\alpha|m\rangle\langle m|\hat{\mu}'_\beta(H)|n\rangle - c.c. \Big)$

$$= \sum_n \rho^{(0)}_{nn} \sum_m \Big(\mu^\alpha_{nm}\, \mu^\beta_{mn}\, e^{i\Omega_{mn}\tau} - c.c. \Big)$$

When computing $\chi^{(1)}$ we have integrals:

$\int_{-\infty}^{0} e^{i(\Omega_{mn} - \omega)\tau} d\tau$. To ensure convergence we add a small imaginary par to the transition freq.:

$$\Omega_{mn} - i\gamma_{mn} \longrightarrow \int_{-\infty}^{0} e^{(i(\Omega_{mn}-\omega)+\gamma_{mn})\tau} d\tau$$

$$= \frac{1}{i(\Omega_{mn}-\omega)+\gamma_{mn}} = \frac{-i}{\Omega_{mn}-\omega-i\gamma_{mn}}$$

Perturbative quantum treatment for a N-level system[2]

We consider N_p/V particles per unit volume, each modeled as a multi-level system. The linear susceptibility is

$$\chi^{(1)}_{\alpha\beta}(-\omega:\omega) = \frac{N_p}{V\varepsilon_0\hbar} = \sum_{n,m}\rho^{(0)}_{nn}\left(\frac{\mu^{\alpha}_{nm}\,\mu^{\beta}_{mn}}{\Omega_{mn}-\omega-i\gamma_{mn}} + \frac{\mu^{\alpha}_{mn}\,\mu^{\beta}_{nm}}{\Omega_{mn}+\omega+i\gamma_{mn}}\right) \tag{7}$$

Far from resonances, when loss is negligible (γ's $= 0$), the linear susceptibility takes a simpler form

$$\chi^{(1)}_{\alpha\beta}(-\omega:\omega) = \frac{N_p}{V\varepsilon_0\hbar}\mathcal{S}_{\mathrm{T}}\left\{\sum_{n,m}\rho^{(0)}_{nn}\left(\frac{\mu^{\alpha}_{nm}\,\mu^{\beta}_{mn}}{\Omega_{mn}-\omega}\right)\right\} \tag{8}$$

where the total symmetrization operator $\mathcal{S}_{\mathrm{T}}$ means that we sum over all possible permutations of the pairs $(\alpha,-\omega)$ and (β,ω).
Often, only a single ground state $n=0$ is populated at room temperature, i.e. $\rho^{(0)}_{nn} = \delta_{n=0}$ and the summation is on m only. Moreover, if $\omega \simeq \Omega_{10}$ (near resonance with state $n=1$) we can simplify the expression to

$$\chi^{(1)}_{\alpha\beta}(-\omega:\omega) \simeq \frac{N_p}{V\varepsilon_0\hbar}\,\frac{\mu^{\alpha}_{01}\,\mu^{\beta}_{10}}{\Omega_{10}-\omega} \tag{9}$$

[2] Butcher & Cotter, *The elements of nonlinear optics*, Ch. 4

Connection with the Lorentz oscillator model

We consider all atoms in the ground state $n = 0$ in an isotropic medium with the excitation field along x, so that $\mu^x_{0m}\mu^x_{m0} = |\mu^x_{0m}|^2 = \frac{1}{3}|\boldsymbol{\mu}_{0m}|^2 = \frac{1}{3}\mu^2_{m0}$. We also define the oscillator strength for the $0 \leftrightarrow m$ transition as

$$f_{m0} = \frac{2m_e\Omega_{m0}\mu^2_{m0}}{3\hbar e^2}$$

where m_e is the electron mass. If we make the approximation $\gamma^2_{m0} \ll \Omega^2_{m0}$ (moderate loss) we can rewrite eq. (7) as

$$\chi^{(1)}_{\alpha\beta}(-\omega:\omega) = \frac{N_p e^2}{V\varepsilon_0 m_e}\sum_{m\geq 1} f_{m0}\frac{1}{\Omega^2_{m0} - \omega^2 - 2i\gamma_{m0}\omega} \tag{10}$$

which is equivalent to the classical expression obtained in the Lorentz oscillator model.