Ch. 2. NONLINEAR POLARIZATION (2ND ORDER PROCESSES)

2.1 Linear Susceptibility (Lorentz Model)

$$\vec{D} = \varepsilon_o \vec{E} + \vec{P} \tag{2.1.1}$$

$$\vec{P} = \varepsilon_o \chi\,(\omega)\,\vec{E} \qquad \chi = susceptibility$$

The response of medium $\vec{P}$ is formed by charged particles, in particular electrons, moving under the action of the field $\vec{E}$. If the displacement of each electron is the same, r, and if all of them are displaced in the direction of the electrical field $\vec{E}$, the polarization of an unity volume of medium with the electron density N is

$$\vec{P} = -Ner\ (\vec{E}/|E\,|) \tag{2.1.2}$$

where e is the charge of electron. Consider the simplest model of polarization based on the assumption that bound electrons are *linear* (or *harmonic*) oscillators (the so called Lorentz model):

$$\frac{d^2 r}{dt^2} + \sigma\,\frac{dr}{dt} + \omega_o{}^2 r = -\,\frac{e}{m}\,\mathcal{E} \tag{2.1.3}$$

where m — the mass of electron,

ω_o — the eigenfrequency of electron oscillation,

σ — a damping parameter.

Consider a harmonic driving field: $\mathcal{E} = E\ cos\,(\omega t - \phi)$, or

$$\mathcal{E} = (1/2)[E(\omega)\,e^{j\omega t} + E^*(\omega)\,e^{-j\omega t}]\ ; \qquad E\,(\omega) = |E\,|\ e^{j\phi} \tag{2.1.4}$$

Substituting this into Eq. (2.1.3) one obtains:

$$r = -\,\frac{e}{m}\,E\,(\omega)\,\frac{e^{j\omega t}}{\omega_o{}^2 - \omega^2 + j\sigma\omega} \tag{2.1.5}$$

Therefore, the *induced* polarization P can be written as follows:

$$P = (1/2)\,\varepsilon_o\,\chi(\omega)\,E\ (\omega)\,e^{j\omega t} + c.c.$$

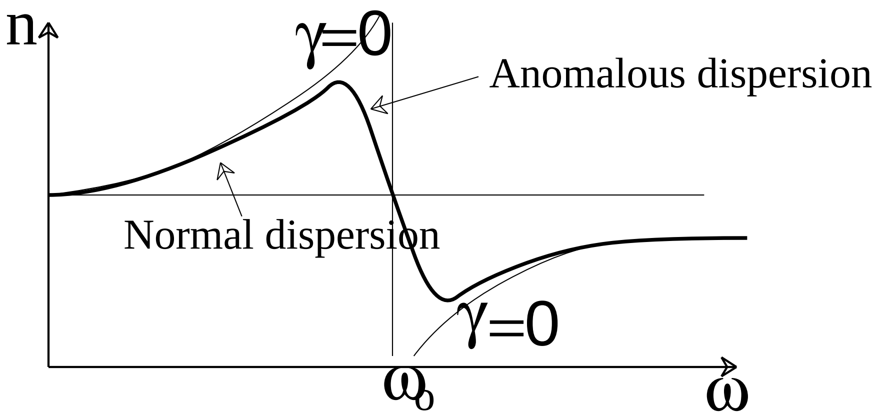
where

$$\chi\,(\omega) = \frac{Ne^2}{\varepsilon_o m}\cdot\frac{1}{\omega_o{}^2 - \omega^2 + j\sigma\omega} \tag{2.1.6}$$

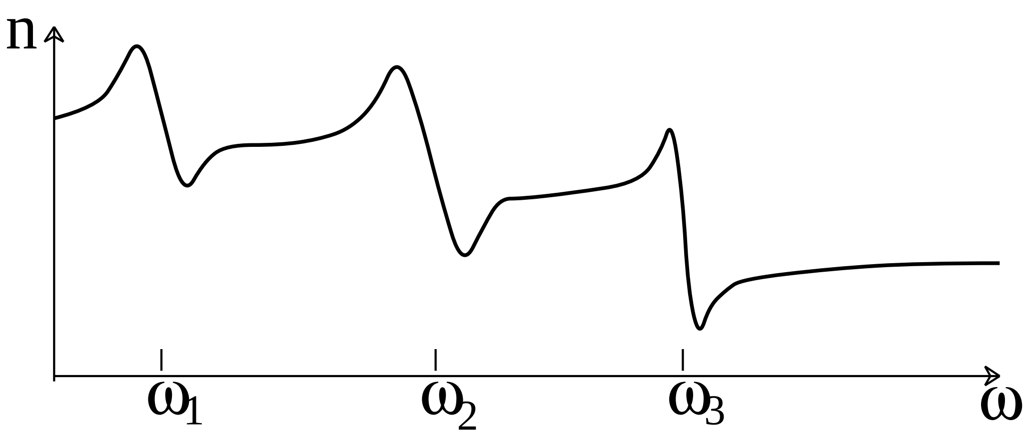
The index of refraction $n = \sqrt{\varepsilon_r}$ is then:

$$n^2 = \varepsilon_r = 1 + \chi = 1 + \frac{Ne^2}{\varepsilon_o m}\cdot\frac{1}{\omega_o{}^2 - \omega^2 + j\sigma\omega} \tag{2.1.7}$$

Damping parameter σ is related to absorption. Absorption is maximal at the resonance ($\omega = \omega_o$).



Usually, a material has many eigenfrequencies



2.2 Anharmonic Oscillator (Second Order Nonlinearity) - Born Approximation

Consider now the Lorentz model with *anharmonicity* (i.e. *nonlinear* oscillator):

$$\frac{d^2r}{dt^2} + \sigma \frac{dr}{dt} + \omega_o^2 r + f(r) = -\frac{e}{m}\mathcal{E} \qquad (2.2.1)$$

where the *nonlinear* function f (r) is assumed to be small $\left[f(r) \ll r\,\omega_o^2\right]$. In the simplest case $f = -\alpha r^2$. What is physical nature of nonlinearity f (r) ? Here are some more or less typical examples:

* Anharmonicity of potential well of electron in atom
* Nonlinear bonds between atom in molecule (for vibrational spectrum)
* Nonlinear restoring force acting upon atoms in crystals
* Saturation of Kerr-effect in liquids
* Saturation of various kinds, (e.g. in two-level system) which lead to changes in χ

* Ultimate nonlinearity: Change of effective mass m due to relativistic effect $m = m_o/\sqrt{1-\upsilon^2/c^2}$. Analogs in semiconductors $m^* = m_o^*/\sqrt{1-\upsilon^2/s_o{}^2}$
* Nonlinearity in semiconductors: shift or saturation of *excitonic levels*.

In the case $f = -\alpha r^2$ one can expand r as:

$$r = r_1 + r_2 + r_3 \ \cdots$$

$r_1 = linear\ term$, $r_2 = first\ order\ term\ in\ \alpha$, etc. For the first two terms one has:

$$\frac{d^2 r_1}{dt^2} + \sigma \frac{dr_1}{dt} + \omega_o{}^2\, r_1 = -\frac{e}{m}\, \mathcal{E} \tag{2.2.2}$$

$$\frac{d^2 r_2}{dt^2} + \sigma \frac{dr_2}{dt} + \omega_o{}^2\, r_2 = -\alpha r_1{}^2 \tag{2.2.3}$$

We now want to have more than one frequency; let us systemize our notations:

$$\mathcal{E} = (1/2)E\ (\omega_1)\ e^{j\omega_1 t} + (1/2)E\ (\omega_2)\ e^{j\omega_2 t} \ldots + c.c$$

We also introduce a notation

$$-\omega_n = \omega_{-n}\ ; \qquad i.e. \qquad E^*(\omega_n) = E(\omega_{-n}) \tag{2.2.4}$$

i.e.

$$\mathcal{E} = (1/2)\sum_n E(\omega_n)\ e^{j\omega_n t} + c.\ c. \tag{2.2.5}$$

We substitute Eq. (2.2.5) into (2.2.2). Assuming

$$r_1 = a_L\ \mathcal{E}^{(L)} \tag{2.2.6}$$

where subscript ‘‘L" stands for ‘‘linear", and having in mind that

$$\frac{dr_1}{dt} = (j/2)a_L \sum_n \omega_n\ E(\omega_n)\ e^{j\omega_n t} + c.\ c.\ ,$$

and

$$\frac{d^2 r_1}{dt^2} = -(1/2)a_L \sum_n \omega_n{}^2\ E(\omega_n)\ e^{j\omega_n t} + c.\ c.\ ,$$

one can with $f = -\alpha r^2$ collect in each part of Eq. (2.2.1) the terms with the same frequencies and obtain that

$$a_L \sum_n E(\omega_n)\ e^{j\omega_n t} = -\frac{e}{m} \sum_n \frac{E(\omega_n) e^{j\omega_n t}}{\omega_o{}^2 + 2j\omega_n\sigma - \omega_n^2}\ , \quad or$$

$$r_1 = -\frac{e}{m} \sum_n \frac{E(\omega_n)\ e^{j\omega_n t}}{\omega_o{}^2 + j\omega_n\sigma - \omega_n{}^2} \tag{2.2.7}$$

It is the same result as in Eq. (2.1.6), generalized now for the case of many eigen-frequencies.

Now we want to find r_2 (nonlinear response). We substitute Eq. (2.2.7) into (2.2.3) and using the following relationship:

$$\left[\sum_n E(\omega_n)\, e^{j\omega_n t}\right]^2 = \sum_n \sum_m E(\omega_n)\, E(\omega_m)\, e^{j(\omega_n + \omega_m)t} \tag{2.2.8}$$

$$(n_{\min} \le m \le n_{\max})$$

solve Eq. (2.2.3):

$$r_2 = -\frac{e^2\alpha}{m^2} \sum_n \sum_m \frac{E(\omega_m)\, E(\omega_n)\, e^{j\,(\omega_m + \omega_n)t}}{F(\omega_o, \omega_n, \omega_m, \sigma)} + c.\ c.\ , \tag{2.2.9}$$

where

$$F = (\omega_o{}^2 + j\omega_n\sigma - \omega_n{}^2)\,(\omega_o{}^2 + j\omega_m\sigma - \omega_m{}^2) \times$$
$$\times \left[\omega_o^2 + j\sigma\,(\omega_n + \omega_m) - (\omega_n + \omega_m)^2\right] \tag{2.2.10}$$

We can express the polarization now in the form of the expansion:

$$P = \sum_{j=1}^{\infty} P_j, \quad with\ P_j = -Ner_j\ . \tag{2.2.11}$$

For linear (complex) polarization we have then:

$$P^{(L)} = \varepsilon_o \sum \chi^{(1)}\,(\omega_n)\, E\,(\omega_n)\, e^{j\omega_n t} \tag{2.2.12}$$

where

$$\chi^{(1)}\,(\omega_n) = \frac{Ne^2}{\varepsilon_o m} \cdot \frac{1}{\omega_o{}^2 + j\sigma\omega_n - \omega_n{}^2}$$

whereas for the *second-order* nonlinear polarization we have

$$P^{NL} = \varepsilon_o \sum_n \sum_m \chi^{(2)}\,(\omega_n, \omega_m)\, E(\omega_n)\, E(\omega_m)\, e^{j(\omega_n + \omega_m)t} \tag{2.2.14}$$

where

$$\chi^{(2)}\,(\omega_n, \omega_m) = \frac{\varepsilon_o^2 \alpha m}{N^2 e^3}\left[\chi^{(1)}(\omega_n)\right]\left[\chi^{(1)}(\omega_m)\right]\left[\chi^{(1)}(\omega_n + \omega_m)\right] \tag{2.2.15}$$

Therefore, we can relate *nonlinear* susceptibility of material to the *linear* susceptibilities at respective frequencies.

2.3 Tensor of Second-Order Nonlinear Susceptibility

Previously, we discussed a scalar case (P, E, and χ were scalars). In more general, 3-D case, χ relates one vector ($\vec{P}^{NL}$) to the product of two vectors ($\vec{E}_j$ and $\vec{E}_k$), and therefore, it becomes a tensor of a third rank. Now, instead of Eq. (2.2.14), one gets

$$P_i\,(\omega_n + \omega_m) = \varepsilon_o \sum_{jk} \sum_{nm} \chi_{ijk}\,(\omega_n + \omega_m;\, \omega_n,\, \omega_m) \times$$

$$\times E_j\,(\omega_n) \times E_k\,(\omega_m)\, e^{j(\omega_n + \omega_m)t} \qquad (2.3.1)$$

(i, j, k - coordinate indices)

$\chi^{(2)}\,(2\omega_1;\, \omega_1,\, \omega_1)$ — second harmonic generation

$\chi^{(2)}\,(\omega_3;\, \omega_1,\, \pm\omega_2)$ — sum and difference frequency generations; parametric amplification

$\chi^{(2)}\,(\omega_1;\, \omega_1,\, 0)$ — dc linear electro-optic effect

$\chi^{(2)}\,(0;\, \omega_1,\, -\omega_1)$ — optical rectifications (*inverse* electro-optic effect)

We will not go into detailed theory of the tensor χ_{ijk} (for more details, see e.g. Zernike & Midwinter, *Applied Nonlinear Optics*); we will, however, briefly discuss some of its main properties.

It was found empirically by Miller, that in analogy with scalar relationship for $\chi^{(2)}$, the formula which relates nonlinear tensor $\chi^{(2)}{}_{ijk}\,(\omega_1;\, \omega_2,\, \omega_3)$ with the tensor of linear susceptibility $\chi^{(1)}{}_{ij}\,(\omega)$ (Miller's rule) is:

$$\chi^{(2)}{}_{ijk}\,(\omega_1;\, \omega_2,\, \omega_3) = \left[\chi^{(1)}{}_{ii}\,(\omega_1)\right] \left[\chi^{(1)}{}_{jj}\,(\omega_2)\right] \left[\chi^{(1)}{}_{kk}\,(\omega_3)\right] \Delta_{ijk} \qquad (2.3.2)$$

where quantity Δ_{ijk} is approximately constant for a great variety of materials. Let us roughly estimate a magnitude of $\chi^{(2)}$ and Δ in crystals with the given lattice spacing $a \approx N^{-1/3}$ where N is the number of atoms per unity volume. We postulate that the nonlinear and linear forces become comparable when the amplitude of oscillations r approaches the lattice spacing a, i.e. in Eq. (2.2.1) with $f = -\alpha r^2$, $\omega_o{}^2 a \approx \alpha a^2$, i.e.

$$\alpha \approx \frac{\omega_o{}^2}{a} \approx \omega_o{}^2\, N^{1/3} \qquad (2.3.3)$$

In the case of second harmonic generation, $\omega_3 = 2\omega_1$ (*since* $\omega_1 = \omega_2$), if $\omega_1 \ll \omega_o$

and $2\omega_1 \ll \omega_o$ (i.e. we are very far from the resonance and below it) one has

$$\chi^{(1)}(\omega_1) \sim \frac{Ne^2}{m\omega_o^2\,\varepsilon_o} \approx \chi^{(1)}(2\omega_1) \tag{2.3.4}$$

and from Eq. (2.2.15)

$$\chi^{(2)}\,(2\omega;\,\omega,\,\omega) \approx \frac{e^3\,N^{4/3}}{m^2\,\omega_o^4\,\varepsilon_o} \tag{2.3.5}$$

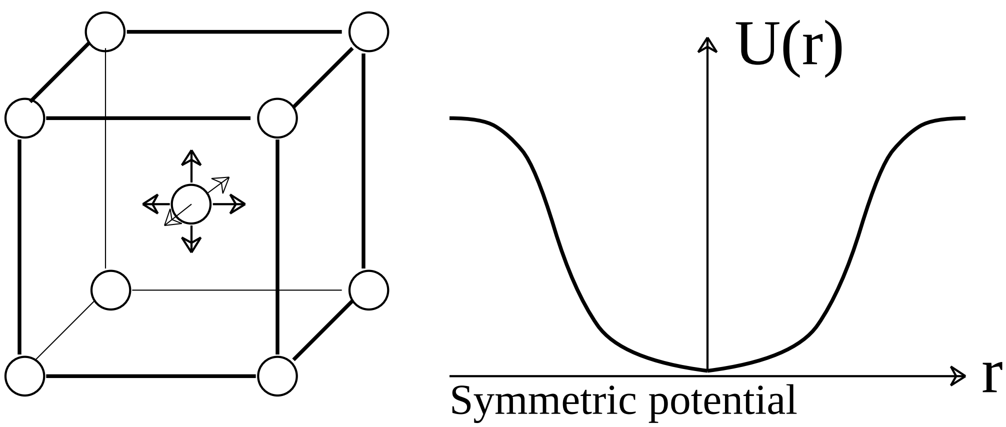
and

$$\Delta \approx \frac{m\,\omega_o^2\,\varepsilon_o^2}{e^3\,N^{5/3}} \tag{2.3.6}$$

For $\lambda_o \sim 1000$Å, $a \sim 2$Å and $m = 9.1 \times 10^{-31}\,kg$, one obtains

$$\Delta \approx 1.2 \times 10^{-13}\,(m/v) \text{ and } \chi^{(2)}\,(2\omega;\,\omega,\,\omega) \approx 2.21 \times 10^{-11}\,(m/v) \tag{2.3.7}$$

One of the most important facts is that in the media with the so called inversion symmetry (or centro-symmetric media) every *even order* susceptibility (in particular *second* order) tensor *vanishes*. To illustrate this, consider oscillations of an atom in the symmetric environment and model it by *one-dimension* motion of a particle in a symmetric potential u(r),



such that acceleration = (external force - internal force) / mass:

$$\rightarrow \frac{d^2r}{dt^2} + \frac{d}{dr}\,[U(r)] = A\cos\omega t \tag{2.3.8}$$

It is well known that if U(r) is a symmetric function, only *odd* harmonics of the frequency ω of pumping force is observable; all *even* harmonics (2ω, 4ω, . . .) vanish. From this, it is clear that there can be no second harmonic generation, parametric amplification or any other $\chi^{(2)}$ process in a medium with inversion symmetry. In particular, they are forbidden in isotropic media like glasses, liquids, and gases (unless there is external force disturbing this symmetry).

More vigorous argument consists in the requirement that in centro-symmetric crystal, a reversal of the signs of E_1 and E_2 must cause a reversal of the sign of P^{NL} and not affect the amplitude. Therefore, using Eq. (2.3.1)

$$P_i = \chi^{(2)}_{ijk} \; E_j \; E_k$$

(we sum over repeated indices), we obtain the following:

$$\chi^{(2)}_{ijk} \; E_j(\omega_1)E_k(\omega_2) = -\chi^{(2)}_{ijk} \; [-E_j(\omega_1)] \; [-E_k \; (\omega_2)]$$

so that $\chi_{ijk} = 0$. Lack of inversion symmetry is also characteristic of *piezoelectric* crystals, so they are expected to display second-order nonlinear effects. In most experiments with second-order nonlinearity, the medium is *transparent* in the domain that includes ω_1, ω_2 ($\omega_{1,2} \ll \omega_o$), and tensor χ_{ijk} does not *depend* on frequency. In this case, as well as for the *second* harmonics generation ($\omega_1 = \omega_2$), no physical significance can be attached to an exchange of E_1 and E_2 in Eq. (2.3.1). Therefore, we can *replace* the subscript jk by a *single* symbol J according to piezoelectric contraction

$$xx: J = 1, \; yy: J = 2, \; zz: J = 3,$$

$$yz = zy: J = 4, \; xz = zx: J = 5, \; xy = yx: J = 6$$

Therefore, the resulting tensor forms a 3×6 matrix that operates on the $E \times E$ column vector to yield $\vec{P}$ (now we introduce coefficient d instead of χ [note: $d = \varepsilon_o \chi/2$], that are more often used in applied nonlinear optics). For **one** input beam, i.e. second harmonic generation with $\omega_1 = \omega_2 = \omega$:

$$\begin{pmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{pmatrix} = \begin{pmatrix} d_{11} \; \ldots\ldots \; d_{16} \\ d_{21} \; \ldots\ldots \; d_{26} \\ d_{31} \; \ldots\ldots \; d_{26} \end{pmatrix} \begin{pmatrix} E_x^2(\omega) \\ E_y^2(\omega) \\ E_z^2(\omega) \\ 2E_z(\omega) \; E_y(\omega) \\ 2E_z(\omega) \; E_x(\omega) \\ 2E_x(\omega) \; E_y(\omega) \end{pmatrix} \qquad (2.3.10)$$

For **two** input beams, e.g. sum and difference frequency generations with $\omega_3 = \omega_1 \pm \omega_2$:

$$\begin{pmatrix} P_x(\omega_3) \\ P_y(\omega_3) \\ P_z(\omega_3) \end{pmatrix} = 2 \begin{pmatrix} d_{11} \; \ldots\ldots \; d_{16} \\ d_{21} \; \ldots\ldots \; d_{26} \\ d_{31} \; \ldots\ldots \; d_{26} \end{pmatrix} \begin{pmatrix} E_x(\omega_1) \, E_x(\omega_2) \\ E_y(\omega_1) \, E_y(\omega_2) \\ E_z(\omega_1) \, E_z(\omega_2) \\ E_z(\omega_1) \; E_y(\omega_2) + E_z(\omega_2) \; E_y(\omega_1) \\ E_z(\omega_1) \; E_x(\omega_2) + E_z(\omega_2) \; E_x(\omega_1) \\ E_x(\omega_1) \; E_y(\omega_2) + E_x(\omega_2) \; E_y(\omega_1) \end{pmatrix} \qquad (2.3.11)$$

(Notice that d_{iJ}'s in generally are functions of frequency. See also A. Yariv, *Quantum Electronics*). In some crystals, the matrix (d) becomes very simple. For example, in

KH_2PO_4 (KDP) the d tensor for second harmonic generation is given by

$$d_{iJ} = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix}$$

and the components of nonlinear polarization are

$$\begin{aligned} P_x &= 2d_{14} E_z E_y \\ P_y &= 2d_{14} E_z E_x \\ P_z &= 2d_{36} E_x E_y \end{aligned} \qquad (2.3.12)$$

As you may find out, the above matrix is just the transpose of the electrooptic tensor for KDP. In fact, tensors for electro-optic and second order nonlinearity obey the same symmetry rules. You can use the table of the electrooptic tensor for various crystal symmetry classes to determine the form of second order tensor by transposing the electrooptic tensor.

2.4 Scalar Formulation of Second Order Nonlinear Polarization

Section 2.3 discusses the cases where the coordinate axes are the principal axes of the crystal. In general, the field may be not lying exact along these axes. If we realign our coordinate axes such that propagation direction is in z direction and the transverse plane is on the xy plane, we can obtain scalar relationship:

$$P(\omega_3) = 2d_{eff} E(\omega_1) E(\omega_2) \quad \text{for } sum-frequency\ generation$$

$$P(2\omega) = d_{eff} E^2(\omega) \text{ for } second-harmonic\ generation. \qquad (2.4.1)$$

In each case, d_{eff} is the effective nonlinear coefficient which can be a combination of d_{iJ}'s and is a function of angles.

The procedure for finding out d_{eff} is as follows: 1) Decompose $\vec{E}$ in term of principal axis directions, 2) Apply Eq. (2.3.10) or Eq. (2.3.11), and 3) Transform nonlinear polarization from principal axes coordinates in terms of the transverse plane. Suppose we have two linearly polarized plane waves with amplitudes E_e and E_o propagating with wave vector $\vec{k}$ making an angle θ with the z axis (optic axis). The plane with the optic axis and the wave vector makes an angle ϕ with the x axis. As a result, E_e is the extra-ordinary wave polarized in $-\hat{\theta}$ direction, and E_o is the ordinary wave polarized in $-\hat{\phi}$ direction.

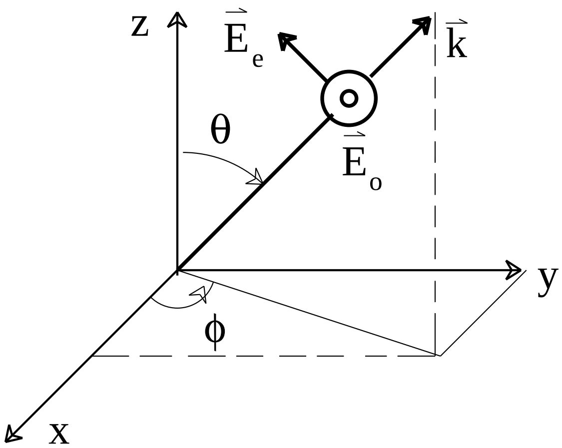
$$\vec{E}_e = -E_e\hat{\theta} = -E_e\ (\cos\theta\cos\phi\hat{x} + \cos\theta\sin\phi\hat{y} - \sin\theta\hat{z}) \qquad (2.4.2)$$

$$\vec{E}_o = -E_o\hat{\phi} = -E_o\ (-\hat{x}\sin\phi + \hat{y}\cos\phi) \qquad (2.4.3)$$

We are interested only in the nonlinear polarization in the transverse plane. (The nonlinear polarization in the propagation direction does not generate a plane wave.)

$$P_e = (P_x\hat{x} + P_y\hat{y} + P_z\hat{z}) \cdot -\hat{\theta} \tag{2.4.4}$$

$$P_o = (P_x\hat{x} + P_y\hat{y} + P_z\hat{z}) \cdot -\hat{\phi} \tag{2.4.5}$$



For example, we input one beam at ω to the KDP example in section 2.3 and assume the beam is polarized in ordinary direction. Substituting Eq. (2.4.3) into Eq. (2.3.12), we obtain:

$$P_x = P_y = 0; \quad P_z = -d_{36} \sin 2\phi \, E_o^2 \tag{2.4.6}$$

Substituting Eq. (2.4.6) into Eq. (2.4.4), we find $P_e = -d_{36} \sin\theta \sin 2\phi \, E_o^2$, i.e. $d_{eff} = -d_{36} \sin\theta \sin 2\phi$.