12

Tensor character of $\chi^{(3)}$

Jones matrix method for polarization

nonlinear ellipse rotation

C. Durfee PHGN 585
Colorado School of Mines

Centro-symmetric media

- For second-order response, the potential must have asymmetry.
- When the binding potential for the electrons is centrally symmetric, the response can still be nonlinear, but the order must be odd (3rd, 5th, etc).
- Consider a central restoring force:

$$\mathbf{F}(\mathbf{r}) = -m\omega_0^2\mathbf{r} + mb(\mathbf{r}\cdot\mathbf{r})\mathbf{r}$$

$$F_i(\mathbf{r}) = -m\omega_0^2 r_i + mbr_j r_j r_i$$

  - force is always directed along $\hat{\mathbf{r}}$ direction
  - At large r, force is less binding.
- As with the non-centrosymmetric potential, perform perturbation expansion.
  - $x^{(2)}$ does not contribute, so $\chi^{(2)}=0$

Classical anharmonic potential: 3rd order response

- Each term for 1st order solution can be a different frequency

$$\ddot{x}^{(3)} + 2\gamma \dot{x}^{(3)} + \omega_0^2 x^{(3)} = b\left(x^{(1)}\right)^3$$

$$\left(\ddot{x}^{(3)}(\omega_q) + 2\gamma \dot{x}^{(3)}(\omega_q) + \omega_0^2 x^{(3)}(\omega_q)\right)e^{-i\omega_q t} = b\sum_{mnp} x^{(1)}(\omega_m)\, x^{(1)}(\omega_n)\, x^{(1)}(\omega_p)\, e^{-i(\omega_m+\omega_n+\omega_p)t}$$

  - Note the m, n, p can all be + or – : for example,
  - Enforce energy conservation, so $\omega_{-2} = -\omega_2$ in summation
- Solution is

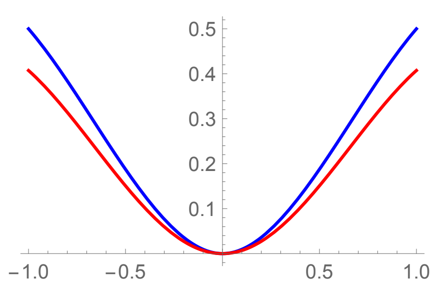
$$\omega_q = \omega_m + \omega_n + \omega_p \rightarrow (mnp)$$

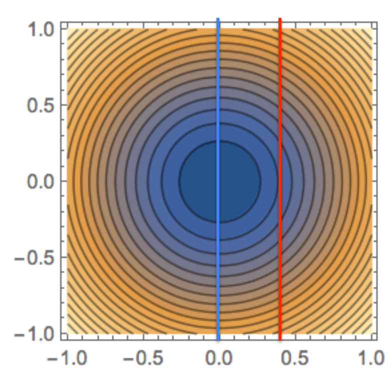
$$\mathbf{r}^{(3)}(\omega_q) = -\sum_{(mnp)} \frac{be^3}{m^3} \frac{\left(\mathbf{E}(\omega_m)\cdot\mathbf{E}(\omega_n)\right)\mathbf{E}(\omega_p)}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

$$\mathbf{P}^{(3)}(\omega_q) = -N\, e\, \mathbf{r}^{(3)}(\omega_q) = +\sum_{(mnp)} N \frac{be^4}{m^3} \frac{\left(\mathbf{E}(\omega_m)\cdot\mathbf{E}(\omega_n)\right)\mathbf{E}(\omega_p)}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

Cross-polarized coupling

- In linear response, the propagation of one polarization component is not affected by another orthogonal component
- At first, it might seem this would remain true for nonlinear propagation if the material is isotropic.
- Contour of binding potential:
  - force in direction of gradient





Calculation of $\chi^{(3)}$

- 3^{rd} order NL polarization is

$$\mathbf{P}^{(3)}(\omega_q) = \sum_{(mnp)} N \frac{be^4}{m^3} \frac{(\mathbf{E}(\omega_m)\cdot\mathbf{E}(\omega_n))\mathbf{E}(\omega_p)}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

- Defined in terms of the susceptibility

$$P_i^{(3)}(\omega_q) \equiv \varepsilon_0 \sum_{jkl}\sum_{(mnp)} \chi_{ijkl}^{(3)}(\omega_q,\omega_m,\omega_n,\omega_p) E_j(\omega_m) E_k(\omega_n) E_l(\omega_p)$$

- $\chi^{(3)}$ is a *tensor*:
  - *i j k l* are *coordinate* indices (1, 2, 3 or *x, y, z*) that correspond to the directions of the *field* polarizations: *i* is output, *j, k, l* are distinct inputs
  - q, m, n, p are frequency indices of the distinct fields
  - All indices can potentially be the same
  - (mnp) in summation means $\omega_q = \omega_m + \omega_n + \omega_p$

$\chi^{(3)}$ tensor

- Convert vector P to summation: e.g.

$$\mathbf{E}(\omega_m)\cdot\mathbf{E}(\omega_n) = \sum_j E_j(\omega_m)E_j(\omega_n) = \sum_{jk} E_j(\omega_m)E_k(\omega_n)\delta_{jk}$$

- 3^{rd} order NL susceptibility is

$$P_i^{(3)}(\omega_q) = \sum_{jkl}\sum_{(mnp)} N \frac{be^4}{m^3} \frac{E_j(\omega_m)E_k(\omega_n)E_l(\omega_p)\delta_{jk}\delta_{il}}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

$$P_i^{(3)}(\omega_q) \equiv \varepsilon_0 \sum_{jkl}\sum_{(mnp)} \chi_{ijkl}^{(3)}(\omega_q,\omega_m,\omega_n,\omega_p) E_j(\omega_m) E_k(\omega_n) E_l(\omega_p)$$

$$\chi_{ijkl}^{(3)}(\omega_q,\omega_m,\omega_n,\omega_p) = \frac{Nbe^4}{\varepsilon_0 m^3} \frac{\delta_{jk}\delta_{il}}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

- Account for "intrinsic permutation symmetry"
  - Fields $E_j(\omega_m)E_k(\omega_n)E_l(\omega_p)$ can be in any order

$$\chi_{ijkl}^{(3)}(\omega_q,\omega_m,\omega_n,\omega_p) = \frac{Nbe^4}{3\varepsilon_0 m^3} \frac{\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

  - 3 terms aren't there b/c of dot product of fields

$\chi^{(3)}$ tensor: isotropic medium

- How can we simplify?

$$\mathbf{P}^{(3)}(\omega_q) = -Ne\mathbf{r}^{(3)}(\omega_q)$$

4th-rank tensor : 81 elements

$$\Rightarrow \mathbf{P}_i^{(3)}(\omega_q) = \sum_{jkl}\sum_{(mnp)} \chi_{ijkl}^{(3)}(\omega_q,\omega_m,\omega_n,\omega_p) E_j(\omega_m) E_k(\omega_n) E_l(\omega_p)$$

$$= D\sum_{jkl} \chi_{ijkl}^{(3)}(\omega_q,\omega_m,\omega_n,\omega_p) E_j(\omega_m) E_k(\omega_n) E_l(\omega_p)$$

where, D : degeneracy factor
(The number of distinct permutations of the frequencies w_m, w_n, w_p)

Only keep elements with an even number for each index

Let's consider the 3rd order susceptibility for the case of an isotropic material.

$\chi_{1111} = \chi_{2222} = \chi_{3333}$ Rotation by 90° with all polarizations parallel

Only 21 nonzero elements :

$$\chi_{1122} = \chi_{1133} = \chi_{2211} = \chi_{2233} = \chi_{3311} = \chi_{3322}$$
$$\chi_{1212} = \chi_{1313} = \chi_{2323} = \chi_{2121} = \chi_{3131} = \chi_{3232}$$
$$\chi_{1221} = \chi_{1331} = \chi_{2112} = \chi_{2332} = \chi_{3113} = \chi_{3223}$$

Rotation by 90° with pairs of perpendicular polarization

and, $\chi_{1111} = \chi_{1122} + \chi_{1212} + \chi_{1221}$

$\chi^{(3)}$ tensor depends on process

Express the nonlinear susceptibility in the compact form :

$$\chi_{ijkl} = \chi_{1122}\delta_{ij}\delta_{kl} + \chi_{1212}\delta_{ik}\delta_{jl} + \chi_{1221}\delta_{il}\delta_{jk}$$

Example: Third-harmonic generation $\chi_{ijkl}(3\omega = \omega + \omega + \omega)$

$\chi_{1122} = \chi_{1212} = \chi_{1221}$ We can permute any of the last 3 indices

$$\Rightarrow \chi_{ijkl}(3\omega = \omega+\omega+\omega) = \chi_{1122}(3\omega = \omega+\omega+\omega) \times (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$$

Example: Intensity-dependent refractive index $\chi_{ijkl}(\omega = \omega + \omega - \omega)$

$\chi_{1122} = \chi_{1212} \neq \chi_{1221}$ $\omega_1=\omega_2$ but $\omega_3 = -\omega_1$: permute only indices 2, 3

$$\chi_{ijkl}(\omega = \omega+\omega-\omega) = \chi_{1122}(\omega = \omega+\omega-\omega) \times (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl}) + \chi_{1221}(\omega = \omega+\omega-\omega)\delta_{il}\delta_{jk}$$

$$\mathbf{P}_i(\omega) = 3\varepsilon_0 \sum_{jkl} \chi_{ijkl}(\omega = \omega+\omega-\omega) E_j(\omega) E_k(\omega) E_l(\omega)$$

$$\mathbf{P}_i(\omega) = 6\varepsilon_0 \chi_{1122} E_i (\mathbf{E}\cdot\mathbf{E}^*) + 3\varepsilon_0 \chi_{1221} E_i^* (\mathbf{E}\cdot\mathbf{E})$$

$$\mathbf{P} = 6\varepsilon_0 \chi_{1122} (\mathbf{E}\cdot\mathbf{E}^*)\mathbf{E} + 3\varepsilon_0 \chi_{1221} (\mathbf{E}\cdot\mathbf{E})\mathbf{E}^*$$ in vector form

A and B representation of NL response

Defining the coefficients, A and B as

$$A = 6\chi_{1122}, \quad B = 6\chi_{1221}$$

$$\mathbf{P} = A\varepsilon_0\left(\mathbf{E}\cdot\mathbf{E}^*\right)\mathbf{E} + \frac{1}{2}B\varepsilon_0\left(\mathbf{E}\cdot\mathbf{E}\right)\mathbf{E}^*$$

(Maker and Terhune's notation)

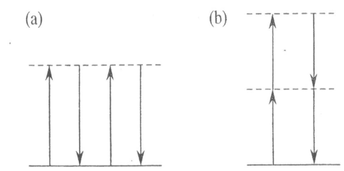


FIGURE 4.2.1 Diagrams (a) and (b) represent the resonant contributions to the nonlinear coefficients A and B, respectively.

The A and B factors depend on the physical mechanisms

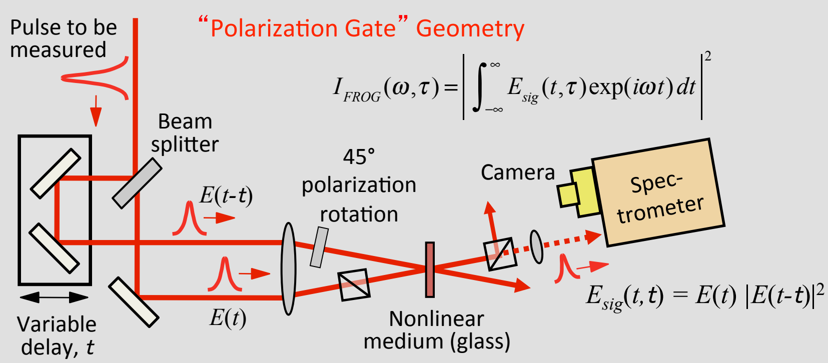
$B/A = 6$: molecular orientation

$B/A = 1$: nonresonant electronic response

$B/A = 0$: electrostriction

Polarization gating

- Tensor nature of $\chi^{(3)}$ allows rotation of polarization by a gating beam

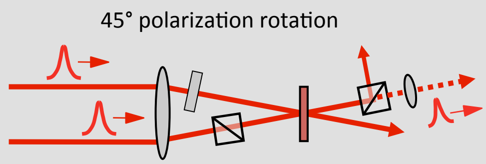


This geometry can also be used as an optical shutter to image fast events.

NL polarization in the interaction

gate $\mathbf{E}_2 = E_2 \frac{1}{\sqrt{2}}(\hat{\mathbf{x}}+\hat{\mathbf{y}})$

probe $\mathbf{E}_1 = E_1 \hat{\mathbf{x}}$



We detect the ***y*** component of the output, *in the direction of probe*:

$$\mathbf{P} = A\left(\mathbf{E}\cdot\mathbf{E}^*\right)\mathbf{E} + \frac{1}{2}B(\mathbf{E}\cdot\mathbf{E})\mathbf{E}^*$$

$$P_y = A\left(\mathbf{E}\cdot\mathbf{E}^*\right)E_{2y} + \frac{1}{2}B(\mathbf{E}\cdot\mathbf{E})E_{2y}^*$$

where

$$\mathbf{E} = \mathbf{E}_1 e^{i\mathbf{k}_1\cdot\mathbf{r}} + \mathbf{E}_2 e^{i\mathbf{k}_2\cdot\mathbf{r}} = \hat{\mathbf{x}}\left(E_1 e^{i\mathbf{k}_1\cdot\mathbf{r}} + \tfrac{1}{\sqrt{2}}E_2 e^{i\mathbf{k}_2\cdot\mathbf{r}}\right) + \hat{\mathbf{y}}\,\tfrac{1}{\sqrt{2}}E_2 e^{i\mathbf{k}_2\cdot\mathbf{r}}$$

$$\mathbf{E}\cdot\mathbf{E}^* = \left(E_1 e^{i\mathbf{k}_1\cdot\mathbf{r}} + \tfrac{1}{\sqrt{2}}E_2 e^{i\mathbf{k}_2\cdot\mathbf{r}}\right)\left(E_1^* e^{-i\mathbf{k}_1\cdot\mathbf{r}} + \tfrac{1}{\sqrt{2}}E_2^* e^{-i\mathbf{k}_2\cdot\mathbf{r}}\right) + \tfrac{1}{2}\left|E_2\right|^2$$

$$= \left|E_1\right|^2 + \tfrac{1}{2}\left|E_2\right|^2 + \tfrac{1}{\sqrt{2}}E_1 E_2^* e^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}} + \tfrac{1}{\sqrt{2}}E_2 E_1^* e^{-i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}} + \tfrac{1}{2}\left|E_2\right|^2$$

$$\mathbf{E}\cdot\mathbf{E} = \left(E_1 e^{i\mathbf{k}_1\cdot\mathbf{r}} + \tfrac{1}{\sqrt{2}}E_2 e^{i\mathbf{k}_2\cdot\mathbf{r}}\right)^2 + \tfrac{1}{2}E_2^{\,2} = E_1^{\,2} e^{2i\mathbf{k}_1\cdot\mathbf{r}} + \tfrac{1}{2}E_2^{\,2} e^{2i\mathbf{k}_2\cdot\mathbf{r}} + \tfrac{2}{\sqrt{2}}E_1 E_2 e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}} + \tfrac{1}{2}E_2^{\,2}$$

Pick output direction and polarization

- Output polarization is in y direction

$$P_y e^{+i\mathbf{k}_1\cdot\mathbf{r}} = A\left(\mathbf{E}\cdot\mathbf{E}^*\right)E_y + \frac{1}{2}B(\mathbf{E}\cdot\mathbf{E})E_y^{\,*} = A\left(\mathbf{E}\cdot\mathbf{E}^*\right)\tfrac{1}{\sqrt{2}}E_2 e^{+i\mathbf{k}_2\cdot\mathbf{r}} + \frac{1}{2}B(\mathbf{E}\cdot\mathbf{E})\tfrac{1}{\sqrt{2}}E_2^{\,*} e^{-i\mathbf{k}_2\cdot\mathbf{r}}$$

- To look for output in the $\mathbf{k}_1$ direction: find combo with E_2 and E_2^*

$$\mathbf{E}\cdot\mathbf{E}^* = \left|E_1\right|^2 + \tfrac{1}{2}\left|E_2\right|^2 + \tfrac{1}{\sqrt{2}}E_1 E_2^* e^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}} + \tfrac{1}{\sqrt{2}}E_2 E_1^* e^{-i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}} + \tfrac{1}{2}\left|E_2\right|^2$$

$$\mathbf{E}\cdot\mathbf{E} = E_1^{\,2} e^{2i\mathbf{k}_1\cdot\mathbf{r}} + \tfrac{1}{2}E_2^{\,2} e^{2i\mathbf{k}_2\cdot\mathbf{r}} + \tfrac{2}{\sqrt{2}}E_1 E_2 e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{r}} + \tfrac{1}{2}E_2^{\,2}$$

$$P_y = A\tfrac{1}{\sqrt{2}}E_1 E_2^*\tfrac{1}{\sqrt{2}}E_2 + \frac{1}{2}B\tfrac{2}{\sqrt{2}}E_1 E_2\tfrac{1}{\sqrt{2}}E_2^*$$

$$= A\tfrac{1}{2}E_1\left|E_2\right|^2 + \tfrac{1}{2}B\,E_1\left|E_2\right|^2 = \tfrac{1}{2}(A+B)E_1\left|E_2\right|^2$$

- E_1 gated by a real quantity, so the phase of P_y is that of E_1

Circular polarization

- Any polarization state can be written as a linear combination of circular basis vectors

$$\mathbf{E} = E_+\hat{\sigma}_+ + E_-\hat{\sigma}_-$$

- Circular polarization basis vectors are a linear combination of x, y components with 90 deg phase shift

$$\hat{\sigma}_+ = \tfrac{1}{\sqrt{2}}\left(\hat{\mathbf{x}} + i\,\hat{\mathbf{y}}\right) \qquad \hat{\sigma}_- = \tfrac{1}{\sqrt{2}}\left(\hat{\mathbf{x}} - i\,\hat{\mathbf{y}}\right)$$

- Properties:

$$\hat{\sigma}_+^* = \hat{\sigma}_- \qquad \text{General case} \qquad \hat{\sigma}_\pm^* = \hat{\sigma}_\mp$$

  - To calculate intensity from vector field: $I \propto |\mathbf{E}|^2 \equiv \mathbf{E}\cdot\mathbf{E}^*$
  - This is how we calculate normalization of unit vectors:

$$|\hat{\sigma}_+|^2 = \hat{\sigma}_+ \cdot \hat{\sigma}_+^* = \hat{\sigma}_+ \cdot \hat{\sigma}_- = 1$$

  - And orthogonality:

$$\hat{\sigma}_+ \cdot \hat{\sigma}_-^* = \hat{\sigma}_+ \cdot \hat{\sigma}_+ = 0$$

NL response to field in circular basis

$$\mathbf{P}^{NL} = A\left(\mathbf{E}\cdot\mathbf{E}^*\right)\mathbf{E} + \frac{1}{2}B\left(\mathbf{E}\cdot\mathbf{E}\right)\mathbf{E}^* \qquad \mathbf{E} = E_+\hat{\sigma}_+ + E_-\hat{\sigma}_-$$

$$\mathbf{E}\cdot\mathbf{E}^* = |E_+|^2 + |E_-|^2$$

$$\begin{aligned}\mathbf{E}\cdot\mathbf{E} &= \left(E_+\hat{\sigma}_+ + E_-\hat{\sigma}_-\right)\cdot\left(E_+\hat{\sigma}_+ + E_-\hat{\sigma}_-\right)\\ &= E_+^2\hat{\sigma}_+\cdot\hat{\sigma}_+ + E_-^2\hat{\sigma}_-\cdot\hat{\sigma}_- + 2E_+E_-\hat{\sigma}_+\cdot\hat{\sigma}_-\\ &= 0 + 0 + 2E_+E_-\end{aligned}$$

$$\begin{aligned}\mathbf{P}^{NL} &= A\left(|E_+|^2 + |E_-|^2\right)\mathbf{E} + \frac{1}{2}B\left(2E_+E_-\right)\mathbf{E}^*\\ &= A\left(|E_+|^2 + |E_-|^2\right)\left(E_+\hat{\sigma}_+ + E_-\hat{\sigma}_-\right) + B\,E_+E_-\left(E_+^*\hat{\sigma}_+^* + E_-^*\hat{\sigma}_-^*\right)\end{aligned}$$

Separate NL polarization into + and - components

$$\mathbf{P}^{NL} = A\left(|E_+|^2 + |E_-|^2\right)\left(E_+\hat{\sigma}_+ + E_-\hat{\sigma}_-\right) + B\,E_+E_-\left(E_+^*\hat{\sigma}_+^* + E_-^*\hat{\sigma}_-^*\right)$$

$$= A\left(|E_+|^2 + |E_-|^2\right)\left(E_+\hat{\sigma}_+ + E_-\hat{\sigma}_-\right) + B\,E_+E_-\left(E_+^*\hat{\sigma}_- + E_-^*\hat{\sigma}_+\right)$$

$$P_+ = A\left(|E_+|^2 + |E_-|^2\right)E_+ + B\,E_+E_-E_-^*$$

$$= A\left(|E_+|^2 + |E_-|^2\right)E_+ + B|E_-|^2\,E_+$$

$$= \left(A|E_+|^2 + (A+B)|E_-|^2\right)E_+$$

$$P_+ = \chi_+E_+ \qquad \chi_+ = A|E_+|^2 + (A+B)|E_-|^2$$

$$P_- = \chi_-E_- \qquad \chi_- = A|E_-|^2 + (A+B)|E_+|^2$$

Tensor response leads to induced optical activity

- "Optically active" materials have a refractive index that is different for R and L circular basis
  - Typically chiral molecules respond this way
- Here, the NL response breaks down into R and L (+ and -) symmetry:

$$n = \sqrt{1 + \chi^{(1)} + 3\chi^{(3)}|E|^2} = \sqrt{n_0^2 + \chi^{NL}}$$

$$n_\pm = \sqrt{n_0^2 + \chi_\pm} \approx n_0\left(1 + \frac{1}{2n_0^2}\chi_\pm\right)$$

$$\chi_+ = A|E_+|^2 + (A+B)|E_-|^2$$

$$\chi_- = A|E_-|^2 + (A+B)|E_+|^2$$

NL propagation: circular input

- If the input is pure circular polarization:

$$\mathbf{E}_{in} = E_+\hat{\sigma}_+ \qquad \mathbf{E}_{out} = E_+ e^{ikz}\hat{\sigma}_+ = E_+ \exp\left[i\, k_0 n_+ z\right]\hat{\sigma}_+$$

$$n_+ = n_0 + \frac{1}{2n_0}\chi_+ = n_0 + \frac{1}{2n_0}\left(A\left|E_+\right|^2 + \left(A+B\right)\left|E_-\right|^2\right)$$

In this case, $E_- = 0$

$$n_+ = n_0 + \frac{1}{2n_0} A\left|E_+\right|^2$$

$$\mathbf{E}_{out} = E_+ \exp\left[i\, k_0\left(n_0 + \frac{1}{2n_0}A\left|E_+\right|^2\right)z\right]\hat{\sigma}_+$$

$$= E_+ e^{ikz}\exp\left[i\, k_0 \frac{A}{2n_0}\left|E_+\right|^2 z\right]\hat{\sigma}_+$$

Here we have a NL phase shift, but no change in polarization

NL propagation, general input

- Treat polarization as a vector $\mathbf{E}_{in} = E_+\hat{\sigma}_+ + E_-\hat{\sigma}_- \Rightarrow \begin{pmatrix} E_+ \\ E_- \end{pmatrix}$
- After propagation, $\mathbf{E}_{out} = \begin{pmatrix} E_+ e^{i k_0 n_+ L} \\ E_- e^{i k_0 n_- L} \end{pmatrix} = e^{i k_0 n_- L}\begin{pmatrix} E_+ e^{i k_0 (n_+ - n_-)L} \\ E_- \end{pmatrix}$

$$\Delta n = n_+ - n_- = \frac{1}{2n_0}\left(A\left|E_+\right|^2 + \left(A+B\right)\left|E_-\right|^2\right) - \frac{1}{2n_0}\left(A\left|E_-\right|^2 + \left(A+B\right)\left|E_+\right|^2\right)$$

$$= \frac{A}{2n_0}\left(\left|E_+\right|^2 - \left|E_-\right|^2\right) + \frac{A+B}{2n_0}\left(\left|E_-\right|^2 - \left|E_+\right|^2\right)$$

$$= \left(\frac{A}{2n_0} - \frac{A+B}{2n_0}\right)\left(\left|E_+\right|^2 - \left|E_-\right|^2\right)$$

$$= \frac{B}{2n_0}\left(\left|E_-\right|^2 - \left|E_+\right|^2\right)$$

For linear polarization input, we have a NL phase shift that is the same for both components, so no change in polarization

NL ellipse rotation

- With elliptical input (neither circular or linear)

$$\mathbf{E}_{out} = e^{i\,k_0 n_- L}\begin{pmatrix} E_+ e^{i\,k_0 \Delta n L} \\ E_- \end{pmatrix} = e^{i\,k_0 (n_- + \Delta n/2)L}\begin{pmatrix} E_+ e^{i\,k_0 \Delta n L/2} \\ E_- e^{-i\,k_0 \Delta n L/2} \end{pmatrix} \quad n_- + \tfrac{1}{2}\Delta n = \tfrac{1}{2}\left(n_+ + n_-\right)$$

- This is what happens when the coordinates were rotated. The ellipticity remains the same.

$$\begin{aligned}
\mathbf{E} &= E_+ \hat{\sigma}_+ e^{i\theta} + E_- \hat{\sigma}_- e^{-i\theta} \\
&= E_+ \tfrac{1}{\sqrt{2}}\left(\hat{\mathbf{x}} + i\,\hat{\mathbf{y}}\right)\left(\cos\theta + i\sin\theta\right) + E_- \tfrac{1}{\sqrt{2}}\left(\hat{\mathbf{x}} - i\,\hat{\mathbf{y}}\right)\left(\cos\theta - i\sin\theta\right) \\
&= E_+ \tfrac{1}{\sqrt{2}}\left\{\left(\hat{\mathbf{x}}\cos\theta - \hat{\mathbf{y}}\sin\theta\right) + i\left(\hat{\mathbf{x}}\sin\theta + \hat{\mathbf{y}}\cos\theta\right)\right\} + \\
&\quad E_- \tfrac{1}{\sqrt{2}}\left\{\left(\hat{\mathbf{x}}\cos\theta - \hat{\mathbf{y}}\sin\theta\right) - i\left(\hat{\mathbf{x}}\sin\theta + \hat{\mathbf{y}}\cos\theta\right)\right\} \\
&= E_+ \tfrac{1}{\sqrt{2}}\left(\hat{\mathbf{x}}' + i\,\hat{\mathbf{y}}'\right) + E_- \tfrac{1}{\sqrt{2}}\left(\hat{\mathbf{x}}' - i\,\hat{\mathbf{y}}'\right) = E_+ \hat{\sigma}'_+ + E_- \hat{\sigma}'_-
\end{aligned}$$

Alternative calculation

$$\mathbf{P}_i^{(3)}(\omega_q) = D\sum_{jkl}\chi_{ijkl}^{(3)}(\omega_q, \omega_m, \omega_n, \omega_p) E_j(\omega_m) E_k(\omega_n) E_l(\omega_p)$$

where, D : degeneracy factor. Here D = 3: (ω, ω, -ω), (ω, -ω, ω), (-ω, ω, ω)

$$\Rightarrow \quad \chi_{ijkl} = \chi_{1122}(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl}) + \chi_{1221}\delta_{il}\delta_{jk}$$

$$\mathbf{P}_i^{(3)}(\omega) = 3\sum_{jkl}\left(\chi_{1122}(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl}) + \chi_{1221}\delta_{il}\delta_{jk}\right) E_j(\omega) E_k(\omega) E_l(-\omega)$$

$$\mathbf{P}_2^{(3)}(\omega) = 3\sum_{jkl}\left(\chi_{1122}(\delta_{2j}\delta_{kl} + \delta_{2k}\delta_{jl}) + \chi_{1221}\delta_{2l}\delta_{jk}\right) E_j(\omega) E_k(\omega) E_l(-\omega)$$

$$\mathbf{P}_2^{(3)}(\omega) = 3\sum_{kl}\begin{matrix}\chi_{1122}\delta_{kl}E_2(\omega)E_k(\omega)E_l(-\omega) + \chi_{1122}\delta_{2k}E_l(\omega)E_k(\omega)E_l(-\omega) \\ +\chi_{1221}\delta_{2l}E_k(\omega)E_k(\omega)E_l(-\omega)\end{matrix}$$

$$\mathbf{P}_2^{(3)}(\omega) = 3\left(2\chi_{1122}E_2(\omega)\left|E_l(\omega)\right|^2 + \sum_{kl}\chi_{1221}\delta_{2l}E_k^2(\omega)E_l(-\omega)\right)$$

$$\mathbf{P}_2^{(3)}(\omega) = 3\left(2\chi_{1122}E_2(\omega)\left|E_l(\omega)\right|^2 + \sum_{k}\chi_{1221}E_k^2(\omega)E_2(-\omega)\right)$$

$$P_2^{(3)}(\omega) = 3\sum_{jkl}\left(2\chi_{1122}E_2E_1E_1^* + 2\chi_{1122}E_1E_2E_1^* + \chi_{1221}E_1E_1E_2^*\right)$$