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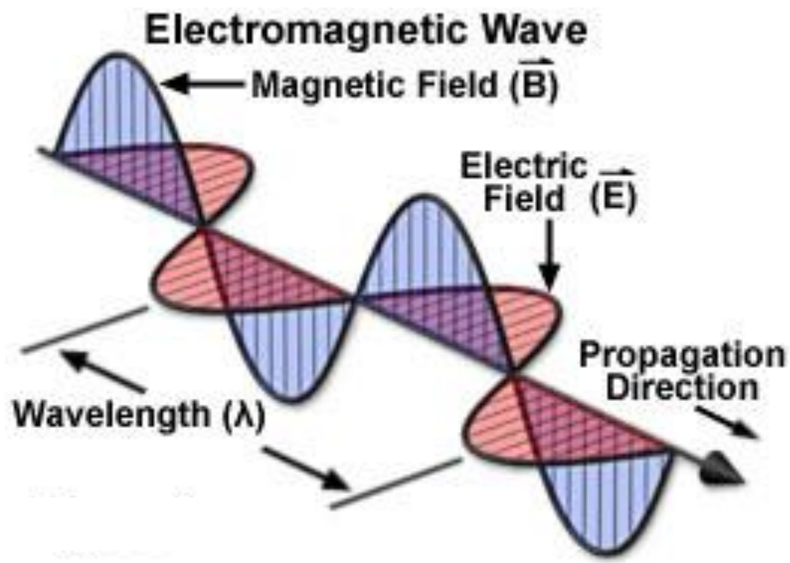
Optical Spectroscopy in Materials Science: Light propagation in materials with broken symmetry

Electromagnetic wave propagation in vacuum

Plane wave solution in free space:

$$\boldsymbol{E}(\boldsymbol{r},t)=\frac{1}{(2\pi)^4}\int d^3\boldsymbol{q}\,d\omega\,\boldsymbol{E}(q,\omega)e^{-i(\omega t-\boldsymbol{qr})}$$

$$\boldsymbol{B}(\boldsymbol{r},t)=\frac{1}{(2\pi)^4}\int d^3\boldsymbol{q}\,d\omega\,\boldsymbol{B}(q,\omega)e^{-i(\omega t-\boldsymbol{qr})}$$



Maxwell's equivations for plane waves:

$$\mathrm{q}\cdot\mathrm{E}=0 \qquad \mathrm{q}\cdot\mathrm{B}=0$$

$$\mathrm{q}\times\mathrm{E}=\omega\mathrm{B} \qquad \mathrm{q}\times\mathrm{B}=-\frac{1}{c^2}\omega\mathrm{E}$$

E, **B** and **q** are orthogonal to each other
Energy flow along **S**||**q**:

$$S=\mathrm{E}\times\frac{\mathrm{B}}{\mu_0}=\frac{q}{\mu_0\omega}\left|E\right|^2$$

The plane wave propagating along **q**||**z** can be described by 4 real parameters, complex E-field amplitudes in the plane perpendicular to **q**:

- intensity ($E_{0x}^2 + E_{0y}^2$)
- overall phase
- polarization (2 parameters)

$$E_0 e^{-i(\omega t-qr)}=\begin{bmatrix}E_{0x}e^{i\delta_x}\\ E_{0y}e^{i\delta y}\end{bmatrix}e^{-i(\omega t-qr)}$$

Polarization of a plane wave

Let’s rotate the (x,y) coordinate system to (x’,y’) in order to satisfy: $\delta_{y'} = \delta_{x'} + \frac{\pi}{2}$

$$\begin{bmatrix} \cos(\theta) & \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{bmatrix} E_0 =$$

$$\begin{bmatrix} \left(E_{0x}\cos(\delta_x)\cos(\theta) + E_{0y}\cos(\delta_y)\sin(\theta)\right) + i\left(E_{0x}\sin(\delta_x)\cos(\theta) + E_{0y}\sin(\delta_y)\sin(\theta)\right) \\ \left(E_{0y}\cos(\delta_y)\cos(\theta) - E_{0x}\cos(\delta_x)\sin(\theta)\right) + i\left(E_{0y}\sin(\delta_y)\cos(\theta) - E_{0x}\sin(\delta_x)\sin(\theta)\right) \end{bmatrix}$$

$$tg(\delta_{x'}) = \frac{E_{0x}\sin(\delta_x)\cos(\theta) + E_{0y}\sin(\delta_y)\sin(\theta)}{E_{0x}\cos(\delta_x)\cos(\theta) + E_{0y}\cos(\delta_y)\sin(\theta)}$$

$$tg(\delta_{y'}) = \frac{E_{0y}\sin(\delta_y)\cos(\theta) - E_{0x}\sin(\delta_x)\sin(\theta)}{E_{0y}\cos(\delta_y)\cos(\theta) - E_{0x}\cos(\delta_x)\sin(\theta)}$$

The above phase convention is satisfy if: $tg(\delta_{y'}) = -\frac{1}{tg(\delta_{x'})}$

...after same algebra... $\boxed{tg(2\theta) = tg(2\Omega)\cos(\delta_x - \delta_y)}$

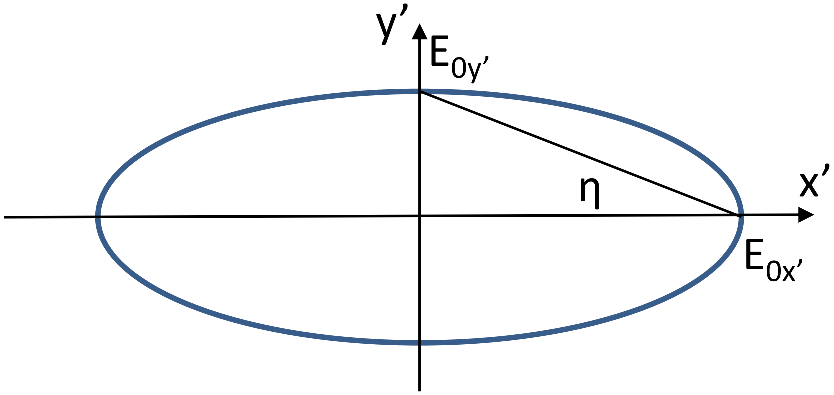
where Ω is defined as $tg(\Omega) = \frac{E_{0y}}{E_{0x}}$

Polarization of a plane wave

Let's rotate the (x,y) coordinate system to (x',y') in order to satisfy: $\delta_{y'} = \delta_{x'} + \frac{\pi}{2}$

In the new basis: $E_0 = \begin{bmatrix} E_{0x'} e^{i\delta_{x'}} \\ E_{0y'} e^{i\delta_{x'} + i\pi/2} \end{bmatrix} = e^{i\delta_{x'}} \begin{bmatrix} E_{0x'} \\ iE_{0y'} \end{bmatrix}$

The time dependence of the fields: $\begin{aligned} E_{x'} &= E_{0x'} \cos(\omega t) \\ E_{y'} &= E_{0y'} \sin(\omega t) \end{aligned}$ $\left(\frac{E_{x'}(t)}{E_{0x'}} \right)^2 + \left(\frac{E_{y'}(t)}{E_{0y'}} \right)^2 = 1$



Ellipticity:

$$tg(\eta) = \frac{E_{0y'}}{E_{0x'}}$$

Polarization of a plane wave

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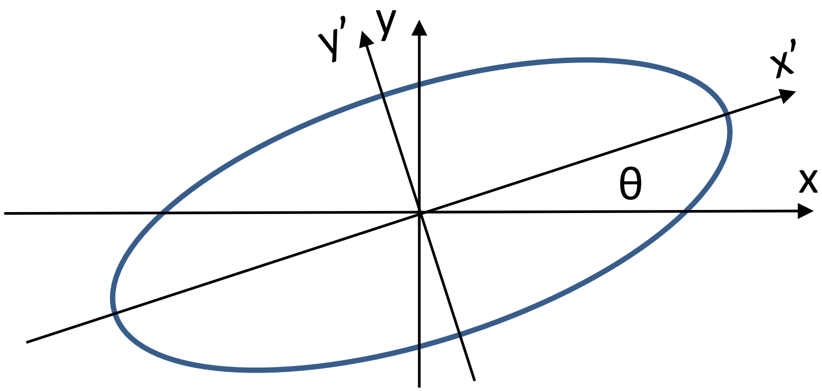


Ellipticity:

$$tg(\eta) = \frac{E_{0y'}}{E_{0x'}}$$

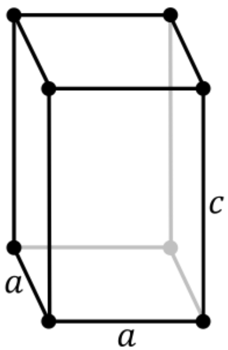
Polarization rotation:

$$tg(2\theta) = tg(2\Omega)\cos(\delta_x - \delta_y)$$

Electromagnetic wave propagation in anisotropic materials

Symmetries of the material → response tensors

eg.: tetragonal symmetry



$$C_2^z \begin{pmatrix}-x\\-y\\z\end{pmatrix} \Rightarrow \begin{matrix}\varepsilon_{xz}=\varepsilon_{zx}=0\\ \varepsilon_{yz}=\varepsilon_{zy}=0\end{matrix}$$

$$\underline{\underline{\varepsilon}} = \begin{bmatrix}\varepsilon_{xx} & 0 & 0\\ 0 & \varepsilon_{xx} & 0\\ 0 & 0 & \varepsilon_{zz}\end{bmatrix}$$

$$C_4^z \begin{pmatrix}y\\-x\\z\end{pmatrix} \Rightarrow \begin{matrix}\varepsilon_{xy}=-\varepsilon_{yx}\\ \varepsilon_{xx}=\varepsilon_{yy}\end{matrix}$$

$$C_2^x \begin{pmatrix}x\\-y\\-z\end{pmatrix} \Rightarrow \varepsilon_{xy}=\varepsilon_{yx}=0$$

$$\mathrm{q}\cdot\varepsilon_0\hat{\varepsilon}\mathrm{E}=0$$

$$\mathrm{q}\times\mathrm{E}=\omega\mu_0 H$$

$$\mathrm{q}\cdot\mu_0 H=0$$

$$\mathrm{q}\times\mathrm{H}=-\omega\varepsilon_0\hat{\varepsilon}\mathrm{E}$$

(assumption μ≈1)

$$q\times(q\times E)=\omega\mu_0(q\times H)$$

$$\boxed{q\cdot(q\cdot E)-q^2E=-\frac{\omega^2}{c^2}\hat{\varepsilon}E}$$

$$e_q=\begin{bmatrix}\sin(\vartheta)\\0\\\cos(\vartheta)\end{bmatrix} \qquad \left(e_q\circ e_q-1+\frac{1}{N^2}\hat{\varepsilon}\right)E=0$$

Electromagnetic wave propagation in anisotropic materials

Solution of the generalized eigenvalue problem:

$$\left| e_q \circ e_q - 1 + \frac{1}{N^2}\hat{\varepsilon} \right| = 0$$

$$\begin{vmatrix} \sin(\vartheta)^2 - 1 + \frac{\varepsilon_{xx}}{N^2} & 0 & \sin(\vartheta)\cos(\vartheta) \\ 0 & -1 + \frac{\varepsilon_{xx}}{N^2} & 0 \\ \sin(\vartheta)\cos(\vartheta) & 0 & \cos(\vartheta)^2 - 1 + \frac{\varepsilon_{zz}}{N^2} \end{vmatrix} = 0$$

$$\left(\sin^2(\vartheta) - 1 + \frac{\varepsilon_{xx}}{N^2}\right)\left(-1 + \frac{\varepsilon_{xx}}{N^2}\right)\left(\cos^2(\vartheta) - 1 + \frac{\varepsilon_{zz}}{N^2}\right) - \sin^2(\vartheta)\cos^2(\vartheta)\left(-1 + \frac{\varepsilon_{xx}}{N^2}\right) = 0$$

$$\boxed{\left(-1 + \frac{\varepsilon_{xx}}{N^2}\right)\left(\frac{\varepsilon_{xx}}{N^2}\frac{\varepsilon_{zz}}{N^2} - \sin^2(\vartheta)\frac{\varepsilon_{zz}}{N^2} - \cos^2(\vartheta)\frac{\varepsilon_{xx}}{N^2}\right) = 0}$$

Solution I.:

$$N = \sqrt{\varepsilon_{xx}}$$

Solution II.:

$$\frac{\cos^2(\vartheta)N^2}{\varepsilon_{zz}} + \frac{\sin^2(\vartheta)N^2}{\varepsilon_{xx}} = 1$$

Electromagnetic wave propagation in anisotropic materials

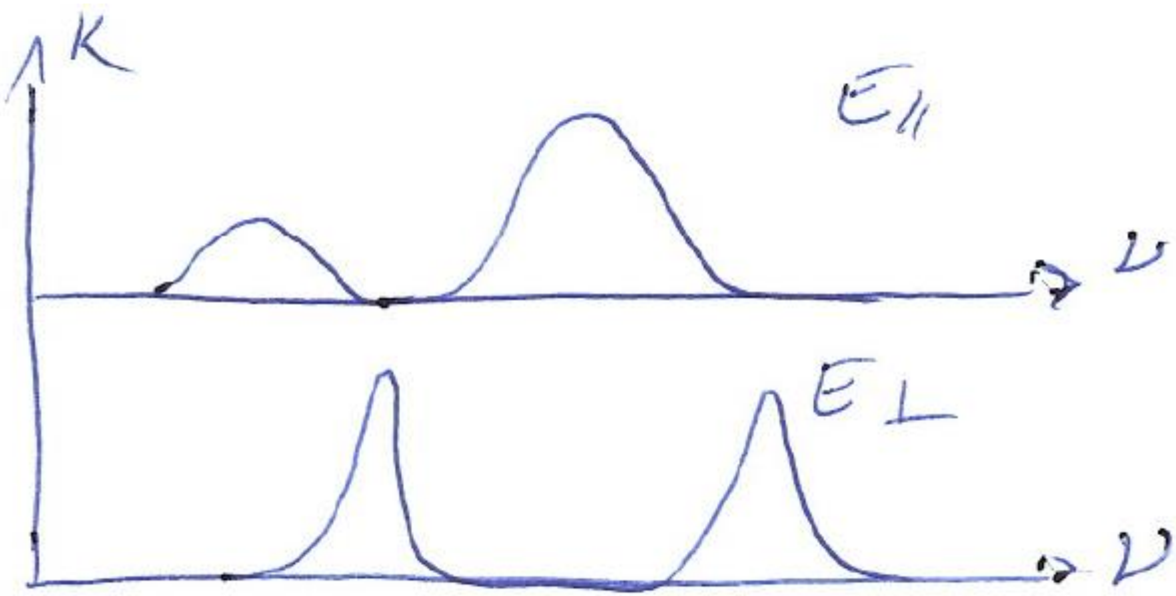
Propagation along the three principal directions:

$q \parallel z \quad \vartheta = 0 \qquad N = \sqrt{\varepsilon_{xx}} \quad \left(\sqrt{\varepsilon_{xx}}\right)$

$q \parallel x$ or $q \parallel y \quad \vartheta = \frac{\pi}{2} \qquad N = \sqrt{\varepsilon_{zz}}\,;\ \sqrt{\varepsilon_{xx}}$

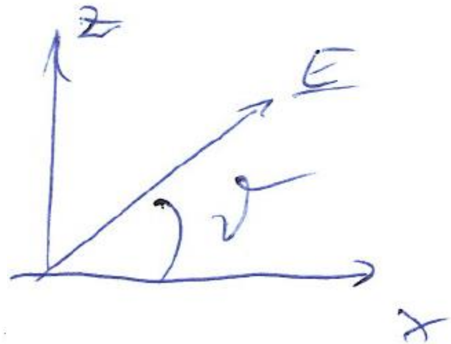
Linear birefringence: $\Delta n = n_{\parallel} - n_{\perp}$

Linear dichroism: $\Delta\kappa = \kappa_{\parallel} - \kappa_{\perp}$



Evolution of the polarization state

Propagation in the tetragonal plane:



$$n_x = \sqrt{\varepsilon_{xx}}$$
$$n_z = \sqrt{\varepsilon_{zz}}$$

$$\begin{bmatrix}\cos\vartheta \\ \sin\vartheta\end{bmatrix} e^{-i\omega t} \qquad y=0$$

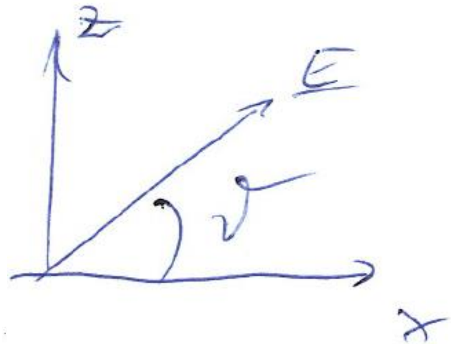
$$\underline{E}(y) = \begin{bmatrix}\cos\vartheta\, e^{i\frac{\omega}{c}n_x y} \\ \sin\vartheta\, e^{i\frac{\omega}{c}n_z y}\end{bmatrix} e^{-i\omega t} \quad \text{@ } y \text{ position}$$

$$\underline{E}(y) = \begin{bmatrix}\cos\vartheta \\ \sin\vartheta\, e^{i\frac{\omega}{c}\underbrace{(n_z - n_x)}_{\Delta n} y}\end{bmatrix} e^{i\frac{\omega}{c}n_x y}\, e^{-i\omega t}$$

Evolution of the polarization from linear to elliptical upon propagation:

Evolution of the polarization state

Propagation in the tetragonal plane:



$$n_x = \sqrt{\varepsilon_{xx}}$$
$$n_z = \sqrt{\varepsilon_{zz}}$$

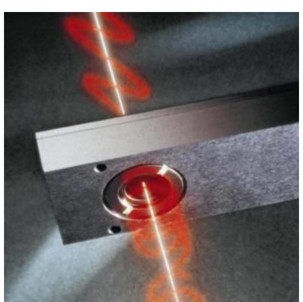
$$\begin{bmatrix}\cos\vartheta \\ \sin\vartheta\end{bmatrix} e^{-i\omega t}$$

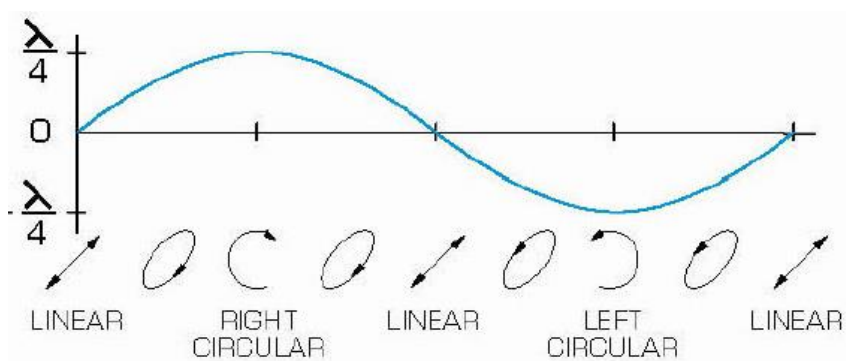
$y = 0$

$$\underline{E}(y) = \begin{bmatrix}\cos\vartheta\, e^{i\frac{\omega}{c}n_x y} \\ \sin\vartheta\, e^{i\frac{\omega}{c}n_z y}\end{bmatrix} e^{-i\omega t}$$

@ y position

$$\underline{E}(y) = \begin{bmatrix}\cos\vartheta \\ \sin\vartheta\, e^{i\frac{\omega}{c}\underbrace{(n_z - n_x)}_{\Delta n}\, y}\end{bmatrix} e^{i\frac{\omega}{c}n_x y}\, e^{-i\omega t}$$





Natural optical activity

Inversion symmetry (i):
polar vectors **r** → -**r**
axial vectors **L**=**rxp** → **L**=(-**r**)x(-**p**)

If the material has inversion symmetry
the magnetoelectric effect is forbidden:

$$\delta \underline{D} = \frac{1}{c}\chi^{em}\underline{H}$$

$$\downarrow i$$

$$-\delta \underline{D} = \frac{1}{c}\chi^{em}\underline{H}$$

$$\Downarrow$$

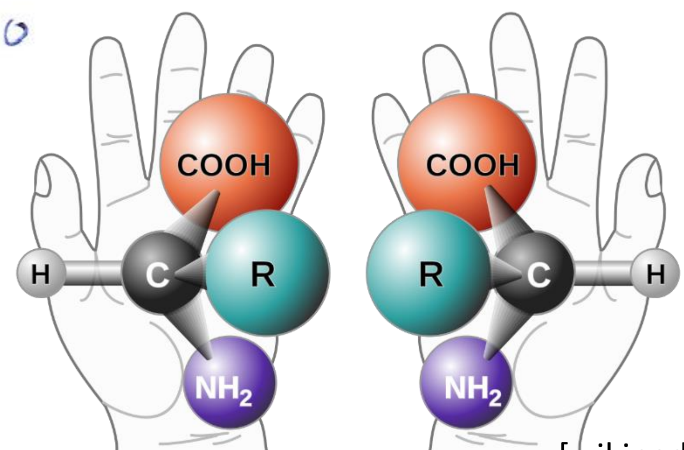
$$\chi^{em} = -\chi^{em}$$

$$\chi^{em} = 0$$

In the lack of inversion symmetry new response functions:

$$\underline{D} = \varepsilon_0 \underline{\underline{\varepsilon}}\,\underline{E} + \frac{1}{c}\underline{\underline{\chi}}^{em}\underline{H}$$

$$\underline{B} = \frac{1}{c}\underline{\chi}^{me}\underline{E} + \mu_0 \underline{\mu}\,\underline{H}$$



[wikipedia]

Natural optical activity

Response functions in an isotropic but non-centrosymmetric material (eq. liquids of chiral molecules, chiral cubic crystals)

$$\underline{D} = \varepsilon_0 \varepsilon \underline{E} + \frac{1}{c} \chi^{em} \underline{H}$$

$$\underline{B} = \frac{1}{c} \chi^{me} \underline{E} + \mu_0 \mu \underline{H}$$

In a time-reversal invariant material
(no magnetic field, non-magnetic material)

$$\alpha := \chi^{em} = -\chi^{me}$$

$$q \times \underline{E} = \omega \underline{B} = \omega \left(\frac{-\alpha}{c} \underline{E} + \mu_0 \mu \underline{H} \right)$$

$$q \times \underline{H} = -\omega \underline{D} = -\omega \left(\varepsilon_0 \varepsilon \underline{E} + \frac{\alpha}{c} \underline{H} \right)$$

$$q \times \underline{E} + \omega \frac{\alpha}{c} \underline{E} = \omega \mu_0 \mu \underline{H}$$

$$q \times \left(q \times \underline{E} + \omega \frac{\alpha}{c} \underline{E} \right) = \omega \mu_0 \mu (-\omega) \left[\varepsilon_0 \varepsilon \underline{E} + \frac{\alpha}{c \cdot \omega \mu_0 \mu} \left(q \times \underline{E} + \omega \frac{\alpha}{c} \underline{E} \right) \right]$$

$$\boxed{q \times (q \times \underline{E}) + 2\alpha \frac{\omega}{c} q \times \underline{E} = -\frac{\omega^2}{c^2} (\varepsilon \mu + \alpha^2) \underline{E}}$$

Natural optical activity

Wave equation for transverse solutions

$$-q^2\underline{E} + 2\alpha\frac{\omega}{c}\,q\times\underline{E} = -\frac{\omega^2}{c^2}(\varepsilon\mu+\alpha^2)\underline{E}$$

For propagation **q**||**z**

$$\left[-\frac{\omega^2}{c^2}N^2 + 2\alpha\frac{\omega^2}{c^2}\begin{bmatrix}0 & -N\\ N & 0\end{bmatrix} + \frac{\omega^2}{c^2}(\varepsilon\mu+\alpha^2)\right]\begin{pmatrix}E_x\\ E_y\end{pmatrix} = 0$$

$$\begin{bmatrix}\varepsilon\mu+\alpha^2-N^2 & -2\alpha N\\ 2\alpha N & \varepsilon\mu+\alpha^2-N^2\end{bmatrix}\begin{pmatrix}E_x\\ E_y\end{pmatrix} = 0$$

$$\boxed{(\varepsilon\mu+\alpha^2-N^2)^2 + (2\alpha N)^2 = 0}$$

Refrective index:

$$N_{\pm} = \sqrt{\varepsilon\mu} \pm i\alpha$$

Eigen modes are circularly polarized:

$$\underline{e}_{\pm} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ \pm i\end{pmatrix}$$

Natural optical activity
Circular birefringence: $\Delta n = n_+ - n_-$
Circular dichroism: $\Delta\kappa = \kappa_+ - \kappa_-$

Natural optical activity

Propagation of eigen modes

$$\underline{E}_{\pm}(\underline{r},t) = \underline{\Delta}_{\pm} E_{0\pm} e^{i\frac{\omega}{c}n_{\pm}z} e^{-i\omega t}$$

Transmission amplitudes

$$t_{\pm} = e^{i\frac{\omega}{c}n_{\pm}z}$$

Transmission matrix in circular basis

$$\begin{bmatrix} e^{i\frac{\omega}{c}n_{+}z} & 0 \\ 0 & e^{i\frac{\omega}{c}n_{-}z} \end{bmatrix} = e^{i\frac{\omega}{c}n_{0}z} \begin{bmatrix} e^{i\frac{\omega}{c}\Delta n z} & 0 \\ 0 & e^{-i\frac{\omega}{c}\Delta n z} \end{bmatrix}$$

$$n_{\pm} = n_0 \pm \Delta n$$

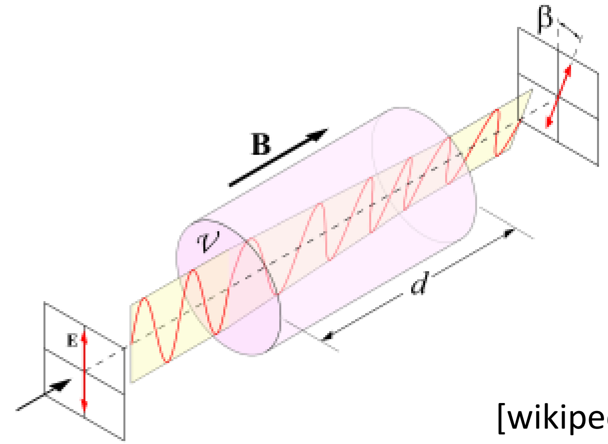
Transmission in linear basis

$$\begin{bmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{bmatrix}$$

Rotation of linear polarization in an isotropic chiral material:

$$\boxed{\alpha = \frac{\omega}{c}\Delta n z}$$

Magneto-optical effects



[wikipedia]

Time-reversal operation (T, ’):
time-reversal even **r** → **r**
time-reversal odd **p** → -**p**

Isotropic or cubic (centro-symmetric) material (SO(3) or O_h)
+
static B-field (∞/mm’m’)

$$\begin{bmatrix} \varepsilon_{xx} & \varepsilon_{xy} & 0 \\ -\varepsilon_{xy} & \varepsilon_{xx} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{bmatrix}$$

Symmetry TC_2^x

$\varepsilon_{xx}(B) = \varepsilon_{xx}(-B)$ ~magnetoresistance

$\varepsilon_{zz}(B) = \varepsilon_{zz}(-B)$

$\varepsilon_{xy}(B) = -\varepsilon_{xy}(-B)$ ~Hall effect

Wave equation

$$q \times (q \times \underline{E}) = \omega \mu_0 q \times \underline{H} = -\frac{\omega^2}{c^2} \underline{\underline{\varepsilon}}\, \underline{E}$$ assuming $\mu = 1$

$$q = q \underbrace{\begin{bmatrix} \sin\vartheta \\ 0 \\ \cos\vartheta \end{bmatrix}}_{\hat{q}}$$

$$\boxed{(\hat{q} \circ \hat{q} - 1)\underline{E} = -\frac{1}{N^2} \underline{\underline{\varepsilon}} \cdot \underline{E}}$$

Magneto-optical effects

In general elliptic solutions:

$$\begin{vmatrix} \frac{\varepsilon_{xx}}{N^2} - \cos^2\vartheta & \frac{\varepsilon_{xy}}{N^2} & \sin\vartheta\cos\vartheta \\ -\frac{\varepsilon_{xy}}{N^2} & \frac{\varepsilon_{xx}}{N^2} - 1 & 0 \\ \sin\vartheta\cos\vartheta & 0 & \frac{\varepsilon_{zz}}{N^2} - \sin^2\vartheta \end{vmatrix} = 0$$

For propagation **q||z,** transverse solutions

$$(\varepsilon_{xx} - N^2)(\varepsilon_{xx} - N^2)\,\varepsilon_{zz} + \varepsilon_{xy}^2\,\varepsilon_{zz} = 0$$

Refrective index:

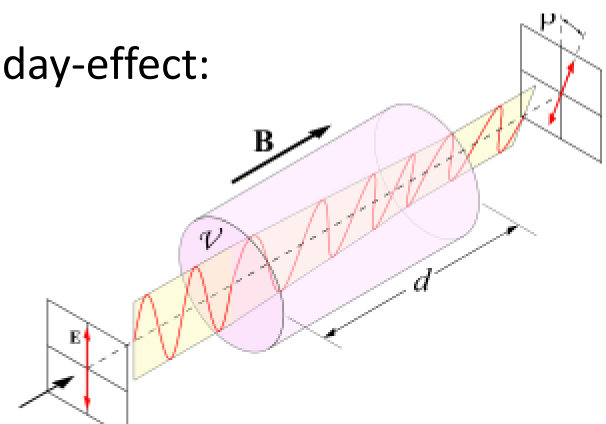
$$N_{\pm} = \sqrt{\varepsilon_{xx} \pm i\,\varepsilon_{xy}}$$

Eigen modes are circularly polarized:

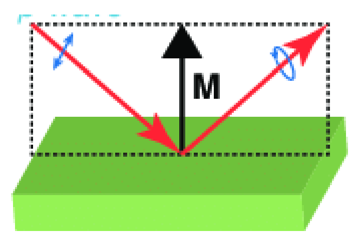
$$\underline{e}_{\pm} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ \pm i \end{bmatrix}$$

Magneto-circular birefringence: $\Delta n = n_+ - n_-$
Magneto-circular dichroism: $\Delta\kappa = \kappa_+ - \kappa_-$

Faraday-effect:

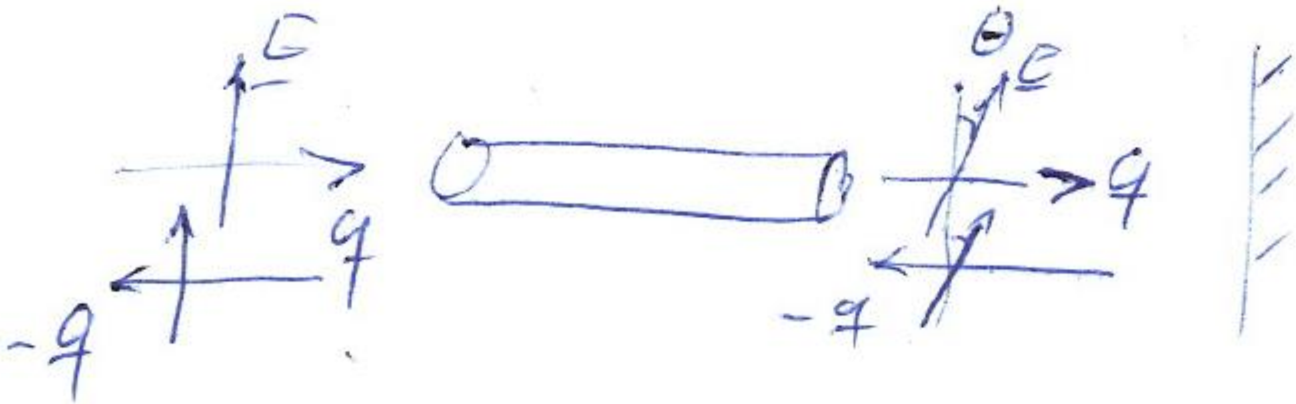


Magneto-optical Kerr-effect:

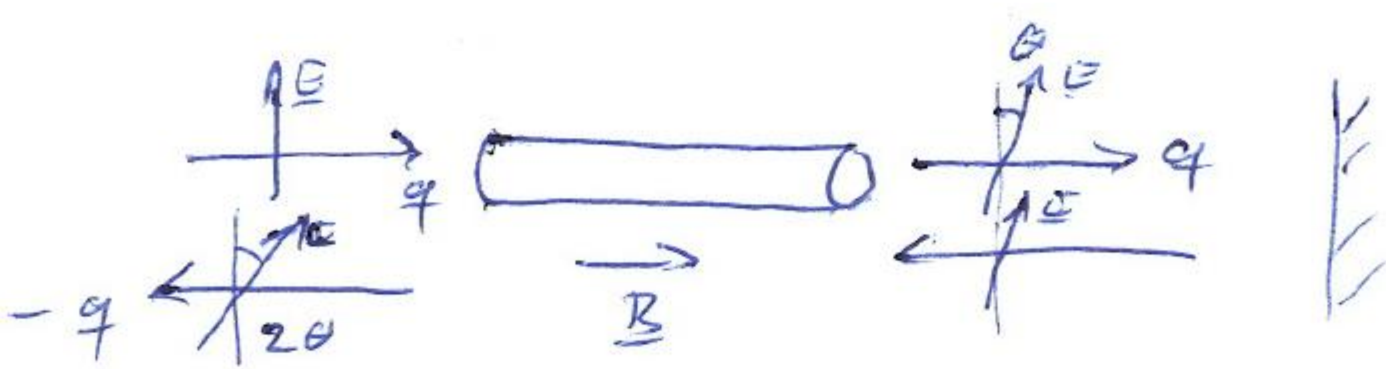


Natural optical activity vs. Faraday rotation

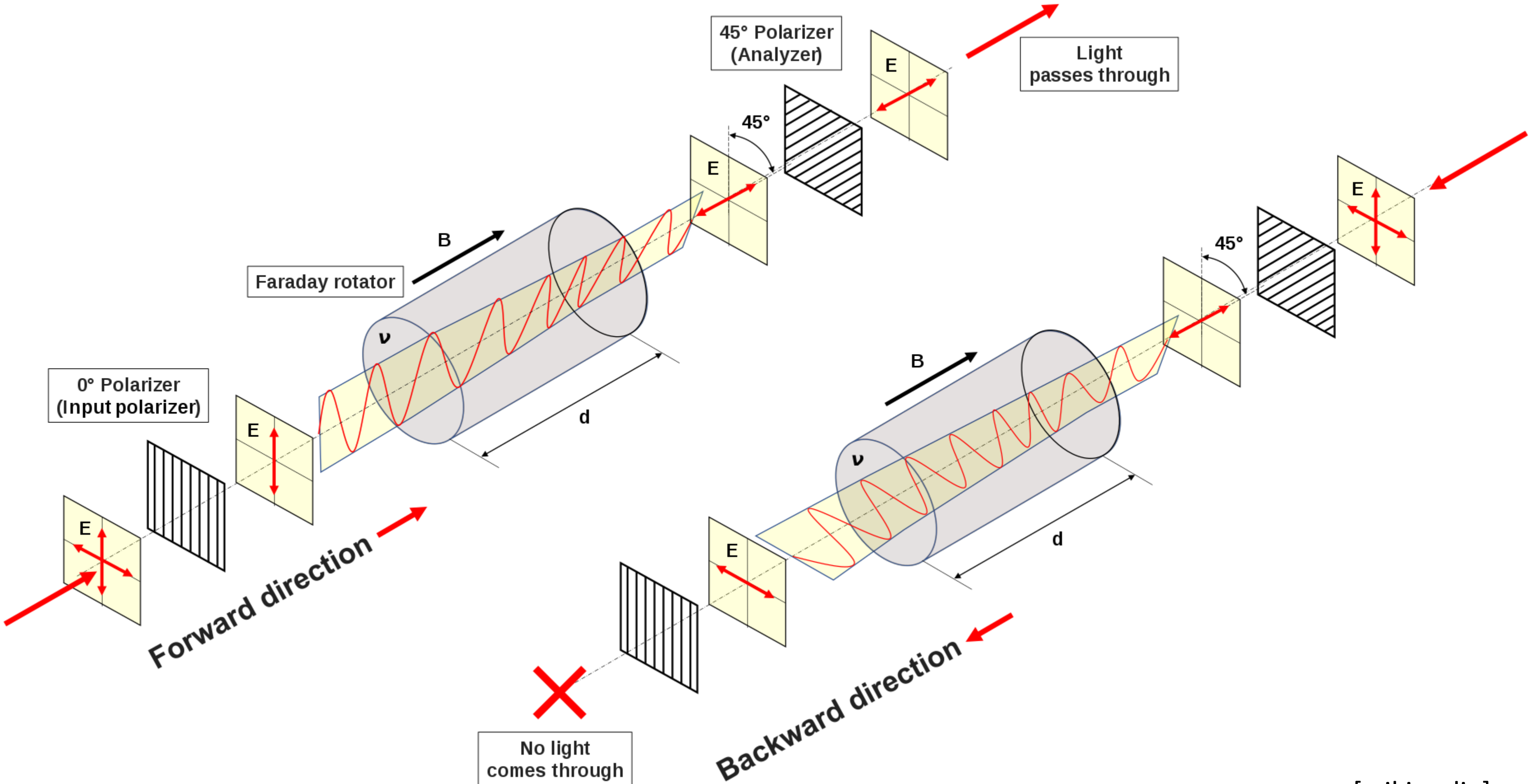
Natural optical activity: ~~i~~ T



Faraday rotation: i ~~T~~



Faraday isolator



[wikipedia]