Chiroptical Spectroscopy

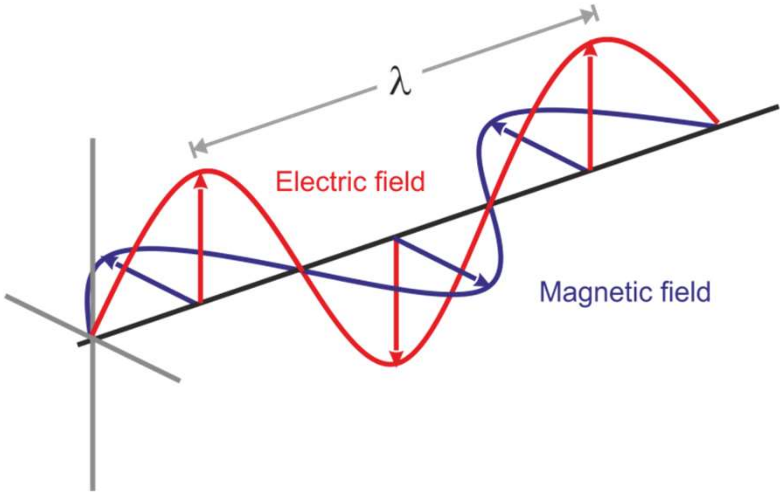
Theory and Applications in Organic Chemistry

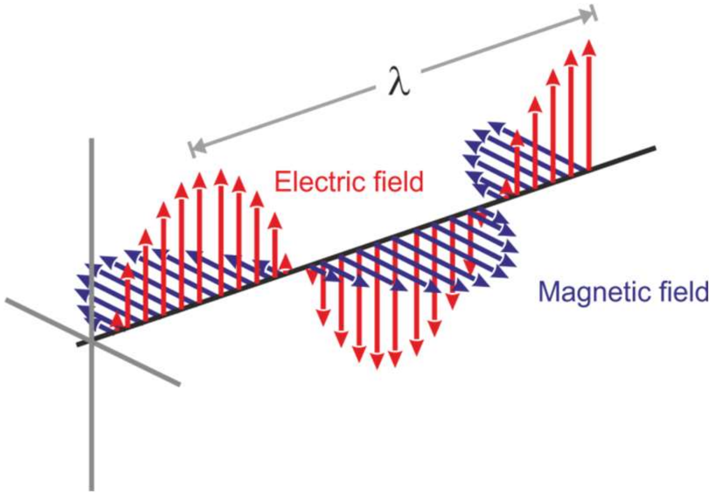
Lecture 2: Polarized light

Masters Level Class (181 041)

Block course, october 2020

Electromagnetic waves



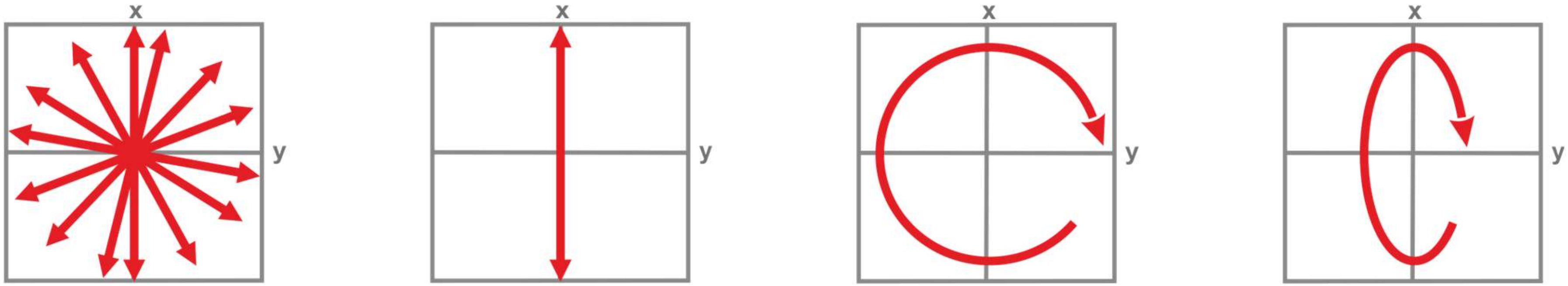


Electromagnetic waves:

- synchronized oscillations of electric and magnetic fields that propagate at the speed of light
- oscillations of the two fields are perpendicular to each other and perpendicular to the direction of energy and wave propagation
- characterized by wavelength/frequency
- In following, we initially only consider the electric field part (convention)!

Classification of polarization

Light (i.e. the electromagnetic wave vector) propagating along the z-axis towards the observer can be



randomly polarized | **linearly polarized** | **circularly polarized** | **elliptically polarized**

Polarization is

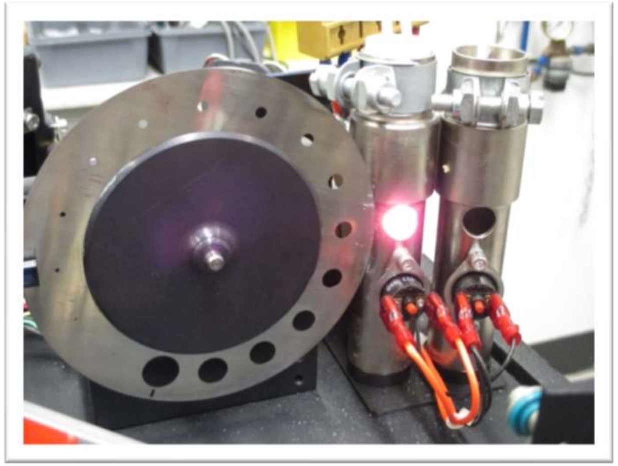
… *a property of waves that describes the orientation of their oscillations*

Light sources in regular spectrometers

Infrared

Globar

- SiC rod, electronically heated to 980-1650 °C
- typically between 5-8 mm x 20-50 mm
- emits radiation with wavelength of 4-15 µm
- spectral behaviour similar to black body



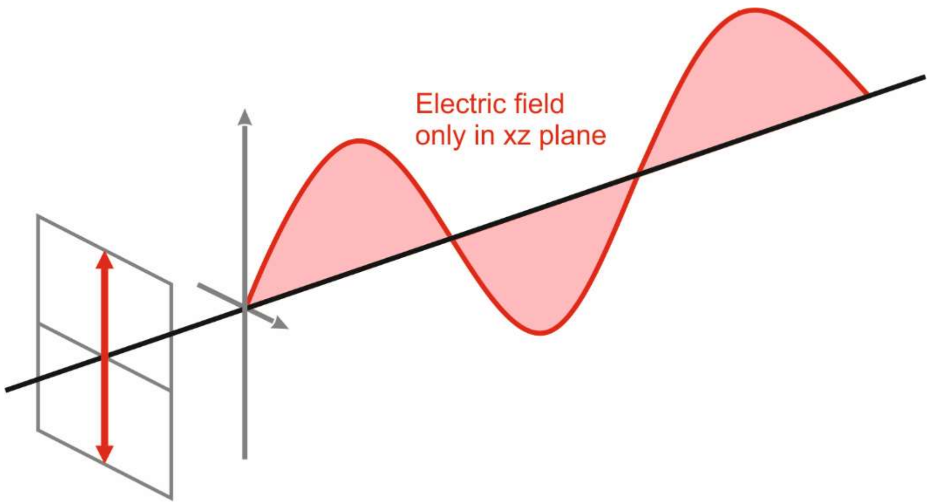
UV/vis

Deuterium arc lamps (190-370 nm)

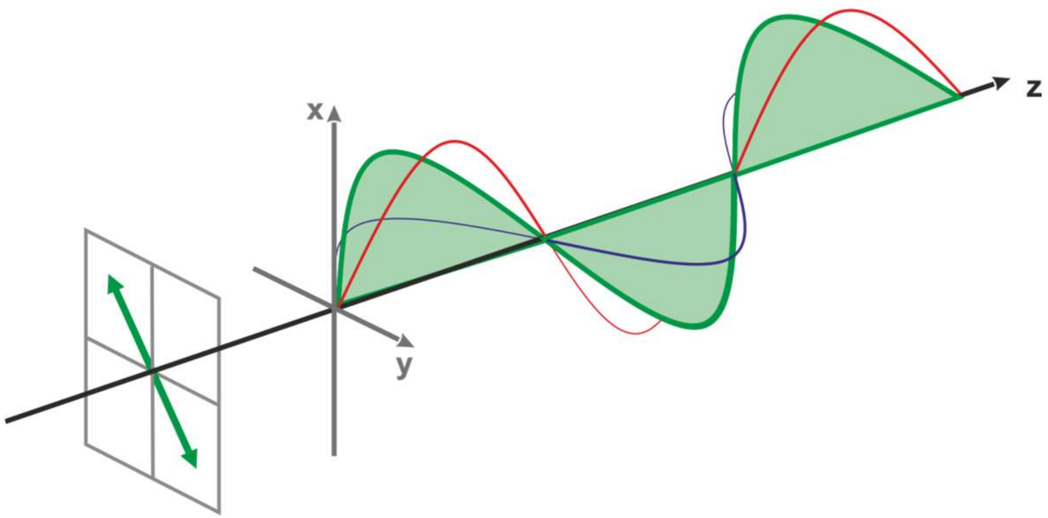
Tungsten halogen (320-1100 nm)

… besides lasers, all UV/IR light sources emit completely randomly polarized light, i.e. a mixture of all kinds of polarizations.

Polarization states: linear polarization



E-field oscillates in a selected plane, here the xz plane, propagating in z-direction.

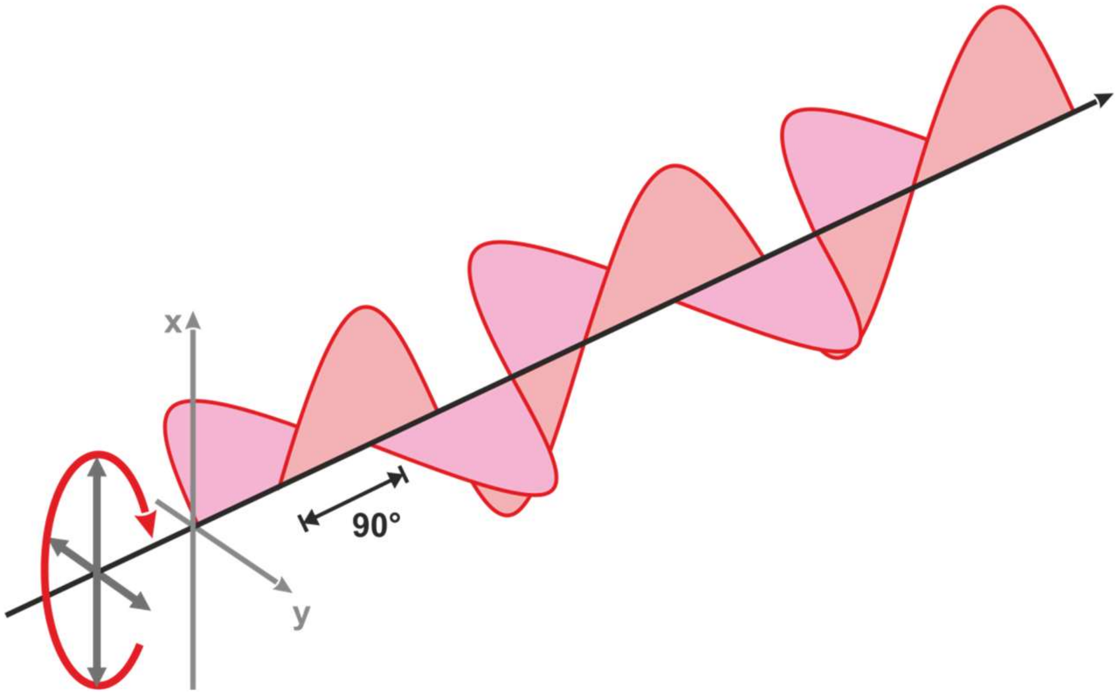


Linear polarized light in any plane can be divided into an **x**- and **y**- component which oscillate in phase (phase shift δ=0)

Example:
-45° polarization

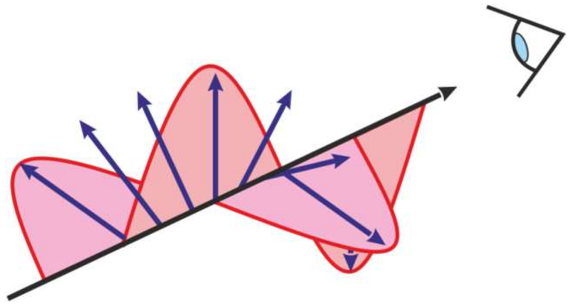
Polarization states: circular polarization

If one introduces a phase shift of exactly ±90° (λ/4) between x- and y-component, circular polarization is obtained:



Polarization states: circular polarization

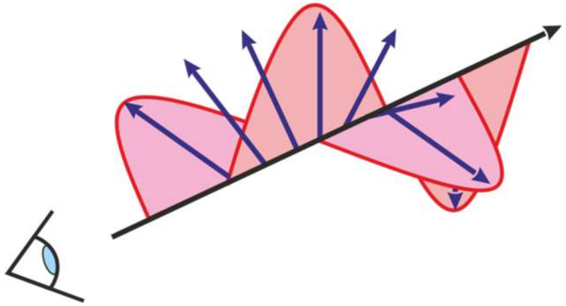
From the observers view towards source:



Electric vector rotates clockwise

➢ **Right circular polarized light**

From view point of source



Electric vector rotates counter-clockwise

➢ **Left circular polarized light**

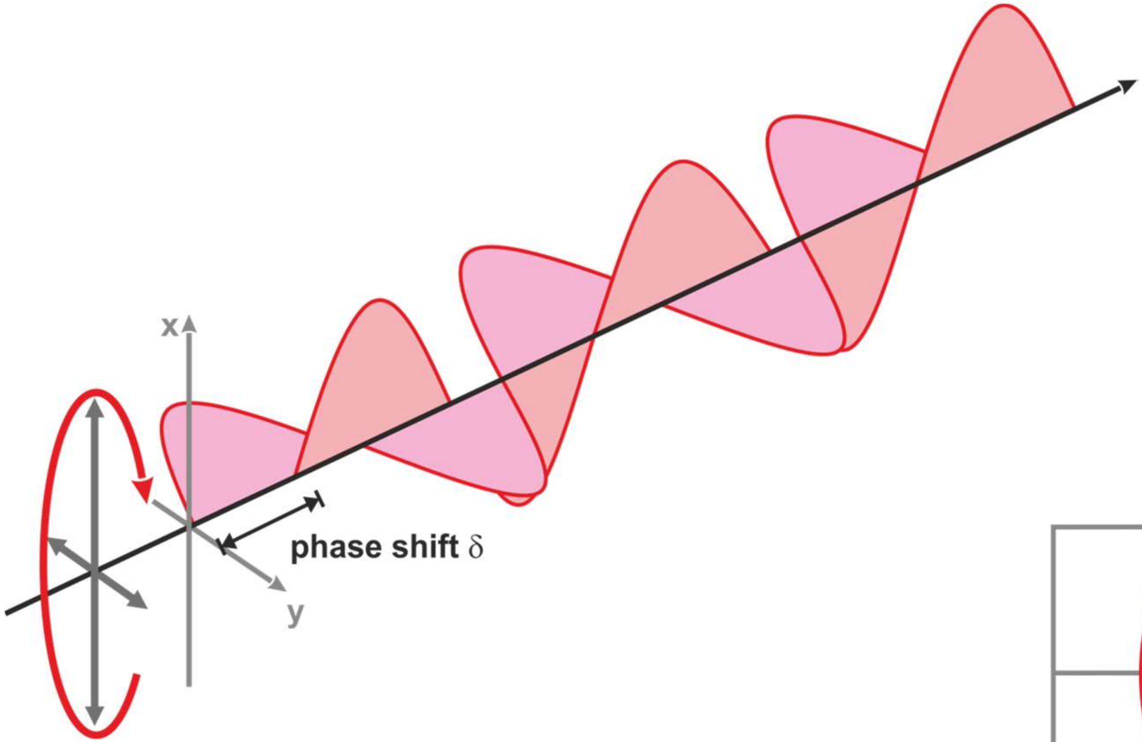
Rule: Point thumb of left or right hand towards source, curl fingers to temporal rotation of field.

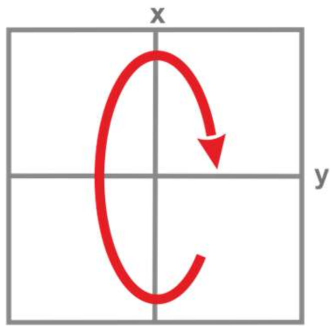
Rule: Point thumb of left or right hand away from source, curling fingers to temporal rotation of field **at given point in space**.

Typically, quantum physics uses the source‘s view, while optics uses the observers‘s view.

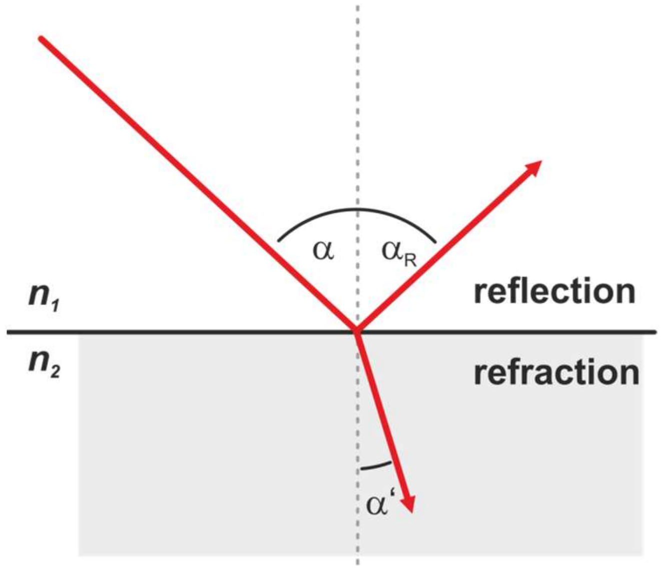
Polarization states: elliptical polarization

Introducing any ***phase shift*** δ and/or ***different amplitudes*** to x- and y-component, elliptical polarization is obtained:





Reflection and refraction



Refractive index:

$$n = \frac{c_0}{c}$$

Snell‘s law (Snellius, 1621):

$$n_1 \cdot \sin \alpha_1 = n_2 \cdot \sin \alpha_2$$

Total reflection ($\alpha > \theta_{crit}$):

$$\theta_{crit} = \arcsin \frac{n_2}{n_1}$$

Birefringence (double refraction)

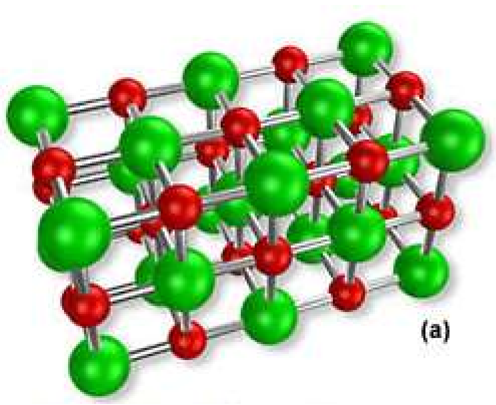
Amorphous material or cubic crystals have a single refractive index

- speed of propagation of an electromagnetic wave is the same in all directions (isotropic medium)

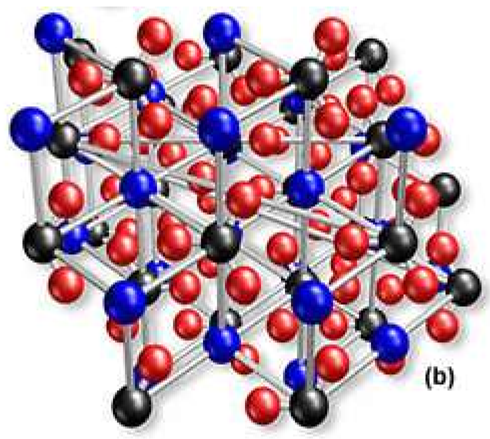
Some minerals (e.g. calcite, quartz) have two distinct indices of refraction

- **birefringant material**

Birefringence relates to the crystal structure of the material

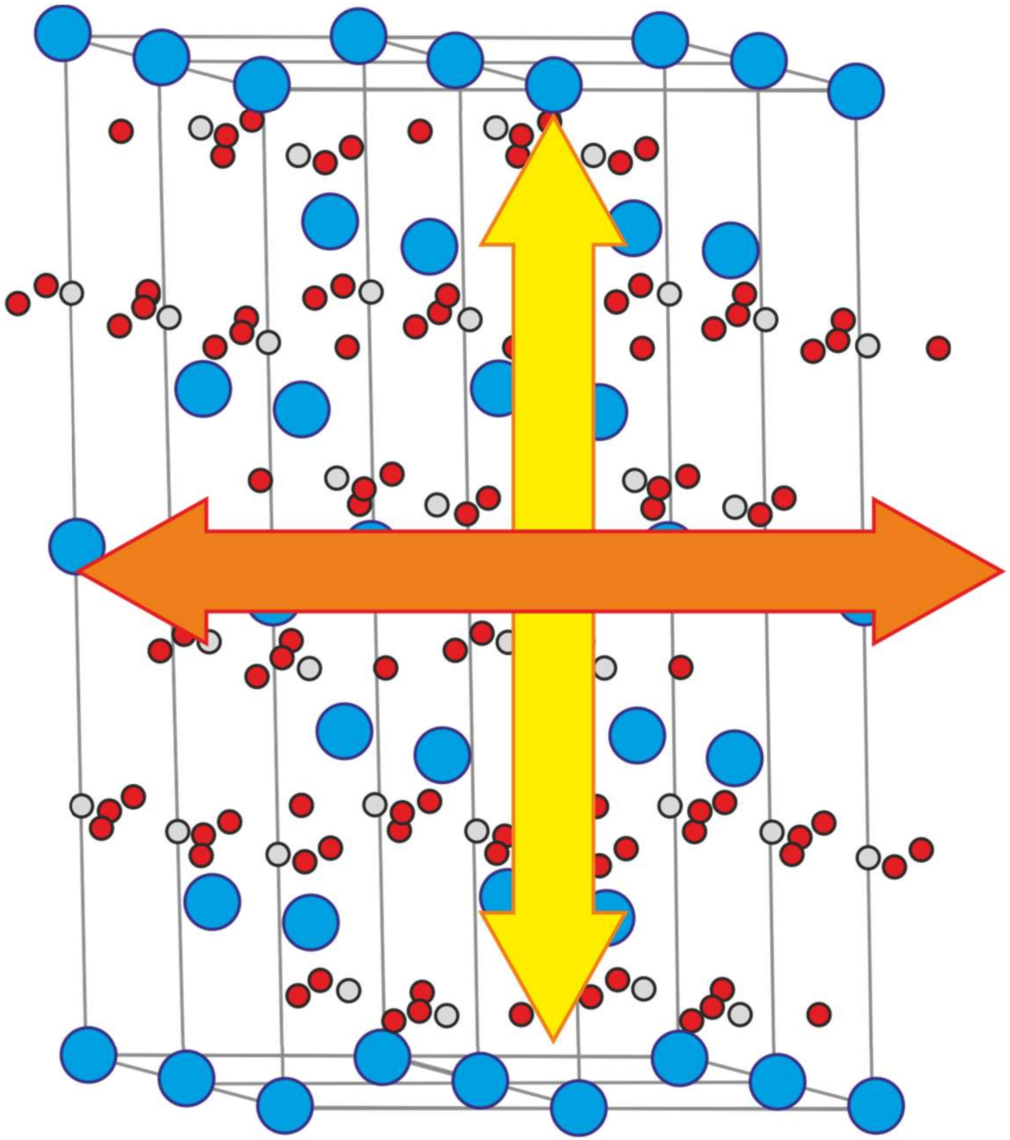


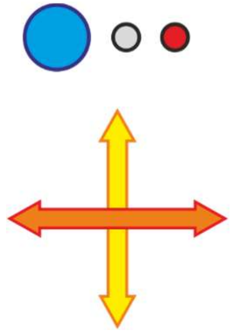
NaCl



$CaCO_3$

Calcite lattice





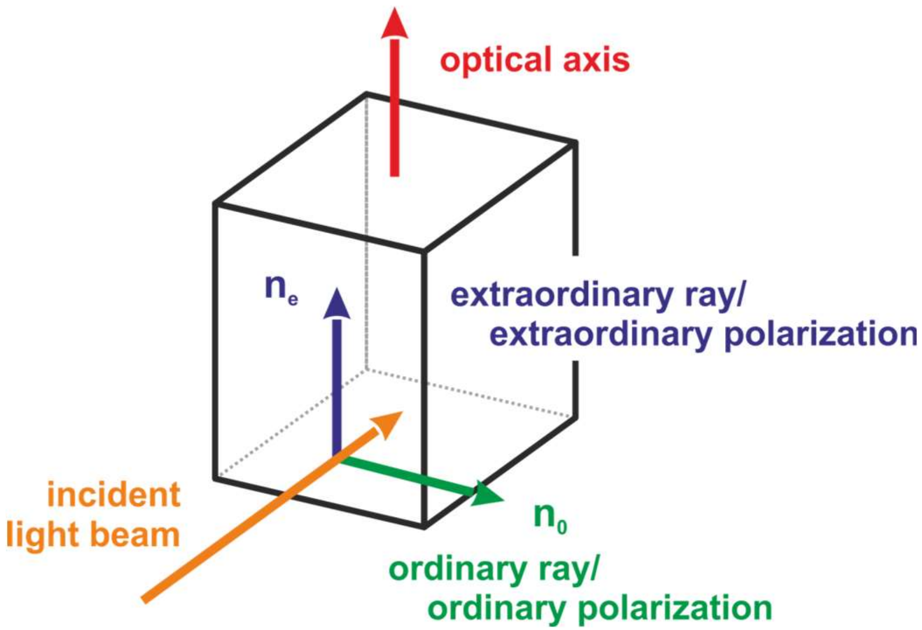
Ca C O

Linear polarized light beams

Perpendicularly polarized light beams exhibit different refractive indices as they interact with different lattice planes and compositions

One defined direction in which both rays have the same index of refraction: optical axis

Birefringence (double refraction)



Uniaxial birefringent crystals have different indices of refraction along crystal principal axes:

n_e: refractive index for light polarized along the **optical axis** of the crystal

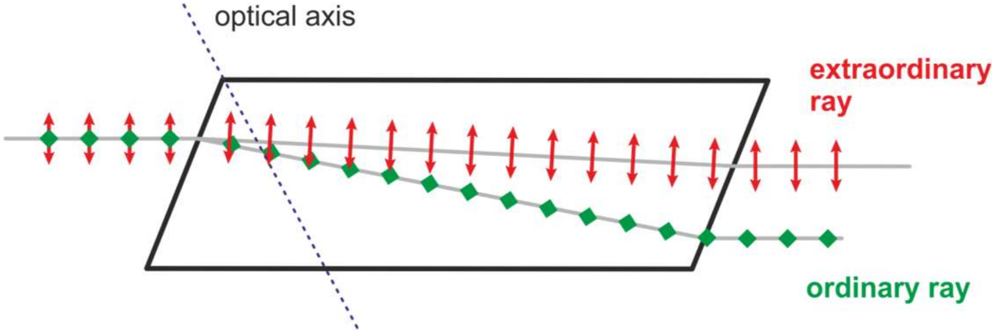
n_o: refractive index for light polarized perpendicular to it.

The axis of the crystal along which a light beam shows the higher propagation speed (= c/n) is called „*fast axis*“, the other one „*slow axis*“.

Refractive indices of some uniaxial birefringent crystals (λ_0=589.3 nm)

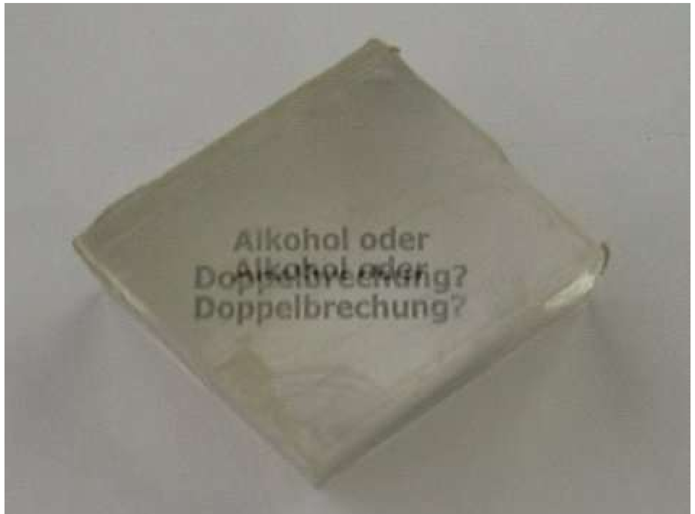
Crystal	n_o	n_e
Tourmaline	1.669	1.638
Calcite	1.6584	1.4864
Quartz	1.5443	1.5534
Sodium nitrate	1.5854	1.3369
Ice	1.309	1.313
Rutile (TiO_2)	2.616	2.903

Birefringence (double refraction)



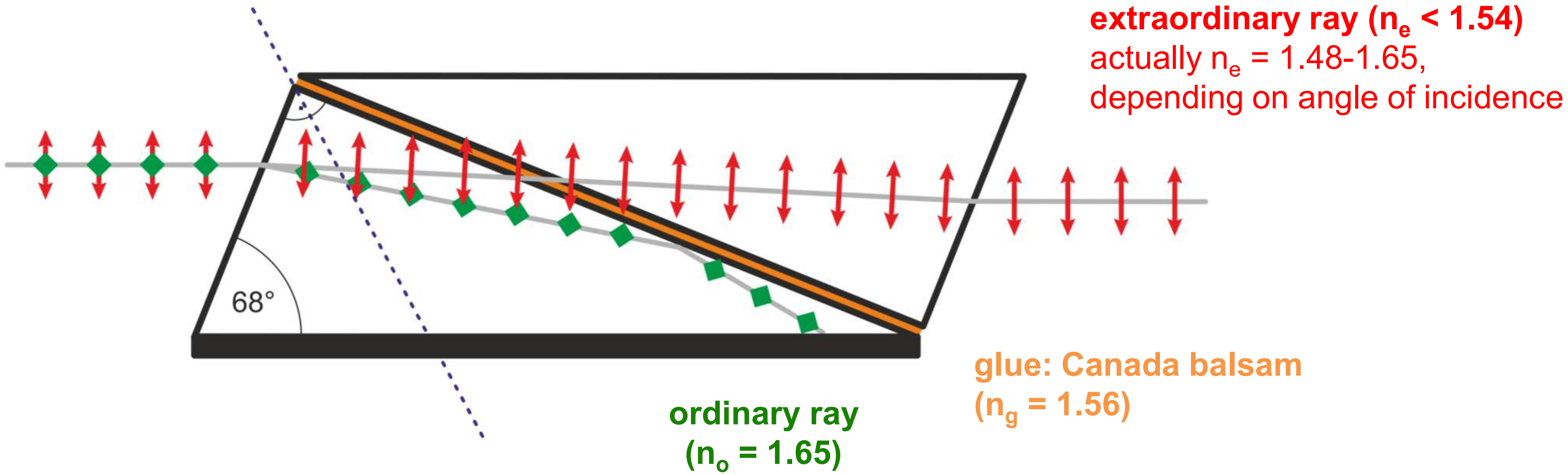
Incident light:
Unpolarized light

Leaving:
Two rays with different polarizations



Picture source: Chemgapedia

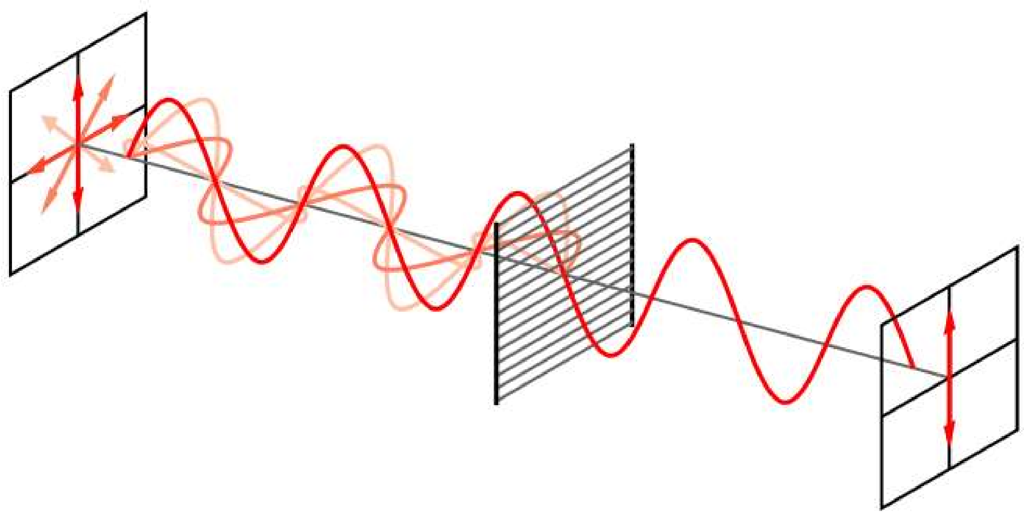
Nicol prism – an effective linear polarizer



As $n_g \approx n_e$, the extraordinary ray is transmitted.

As $n_g < n_o$, the ordinary ray is totally reflected and absorbed by dark wall.

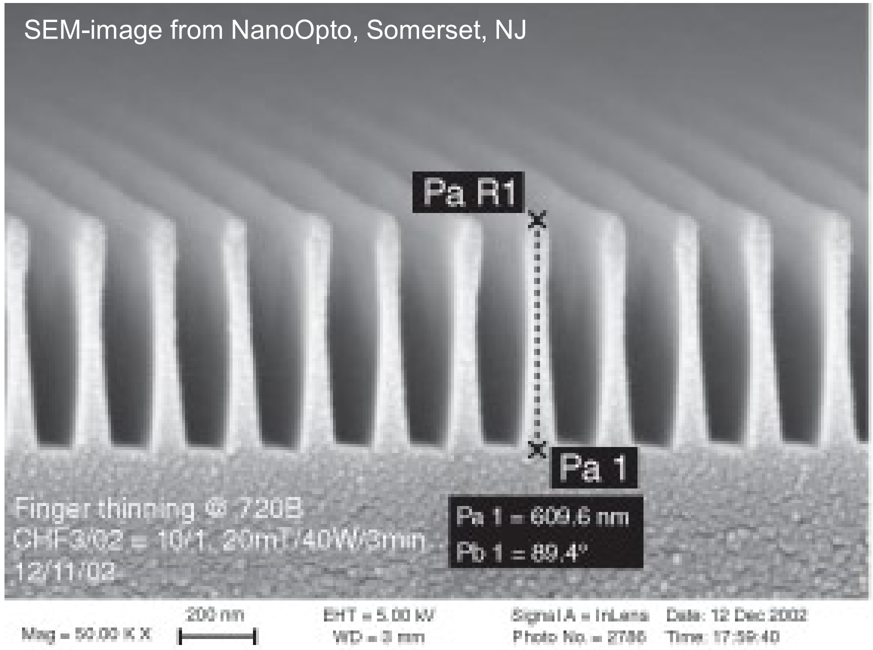
Wire grid polarizers



- Waves hitting the polarizer with their electric field vector parallel to the grid lines induce oscillation of electrons in metal wires:
  - **reflection of the wave**

- Waves hitting the polarizer with their electric field vector perpendicular to the grid lines show weak to no interaction with the grid
  - **transmission of the wave**

Wire grid polarizers



SEM-image from NanoOpto, Somerset, NJ

Thin metal grid coated on support which is transparent in the spectral range of interest.

Polarization works best if distance between grid wires is smaller than wavelength of the light.

Wire grid polarizers work best for microwave, far- and mid-IR.

For IR spectroscopy:

Coatings on KRS-5

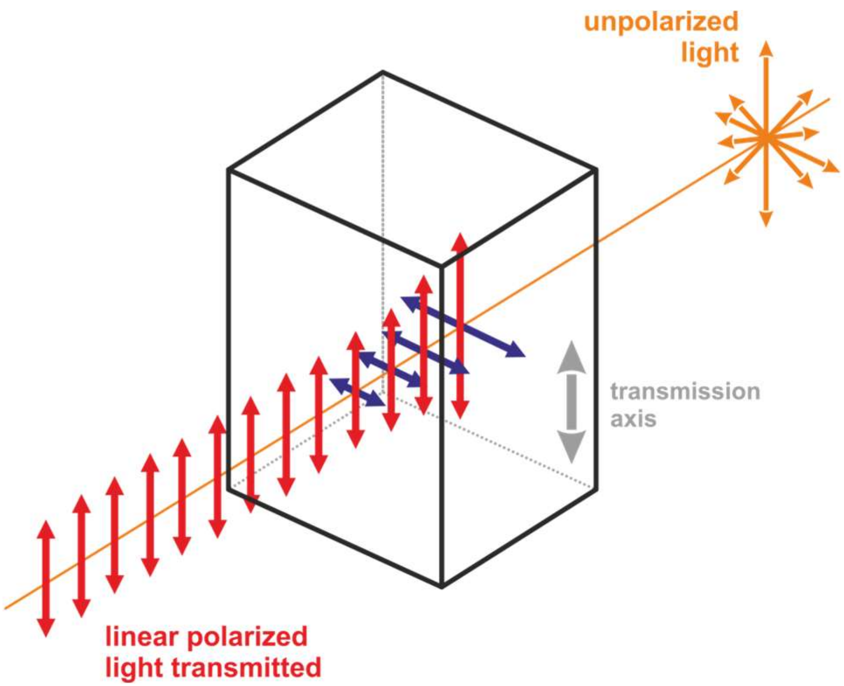
(thallium bromo iodide)

Dichroic materials

Some materials absorp more light of one particular polarization state than of the other. This anisotropy in absorption is called dichroism.

- Complete absorption of one linear component of the light
- Partial transmission of the perpendicular component

Typical materials:
some minerals (e.g. tourmaline), polymer films (e.g. polaroid), …

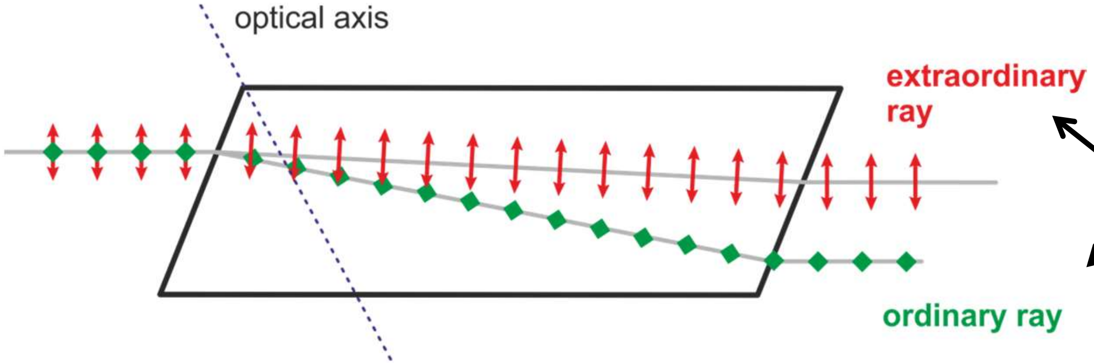


Malus law:

$$I = I_0 \cdot \cos^2 \theta_i$$

with θ_i being the difference between the angle of polarization of incident light and the transmission axis of the polarizer

Wave plate (retarder)



exiting with phase shift!

<u>Idea:</u> Light polarized parallel to *fast axis* leaves the crystal before the light polarized along the *slow axis*.

$$\Delta\varphi = \frac{2\pi}{\lambda} \cdot d \cdot (n_{slow} - n_{fast})$$

➢➢ Choose the thickness of the crystal plate wisely, then you can induce phase shifts of $\lambda/4$ or $\lambda/2$.

Photoelasticity

By applying mechanical stress, some materials become optically anisotropic.

This phenomenon is referred to as photoelasticity, stress birefringance, or mechanical birefringance.

Photoelastic modulator (PEM)

Photoelasticity is key principle for **photoelastic modulation**

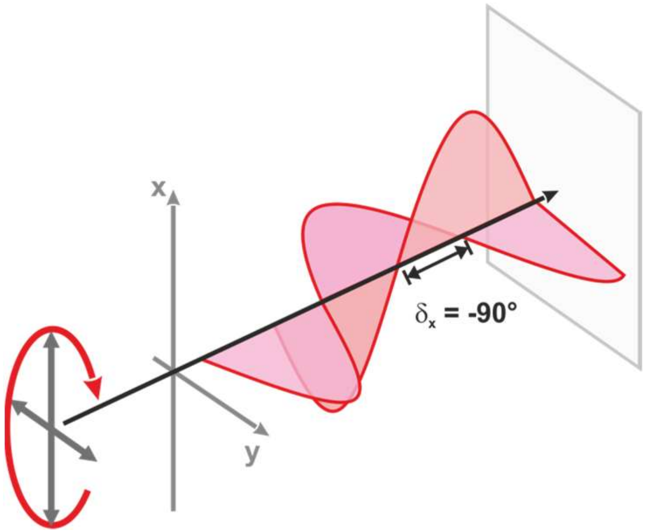
A quartz piezoelectric transducer induces a vibration to a fused silica bar which shows a natural resonant frequency of ~50 kHz. This bar is attached to the photoelastic material.

In case of IR-PM, a ZnSe crystal is used as photoelastic material.

Retardation becomes time dependent:

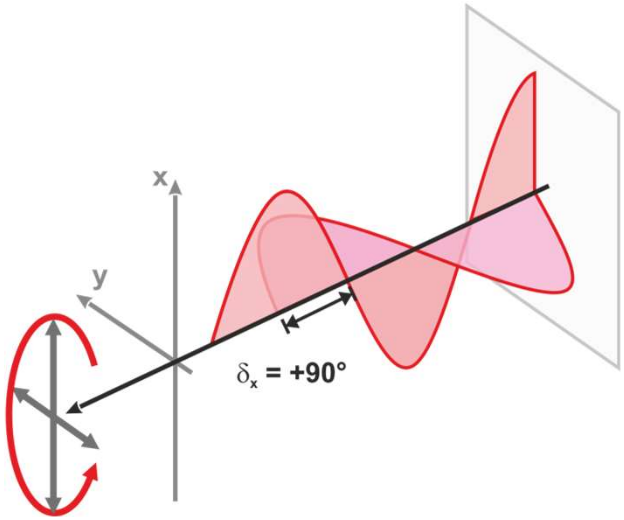
$$\varphi(t) = \frac{2\pi}{\lambda} \cdot d \cdot [n_x(t) - n_y(t)]$$

Polarized light and mirrors: Circular polarization



Angle of incident exactly perpenticular to mirror plane:

+y-component arrives first,
+x-component arrives second

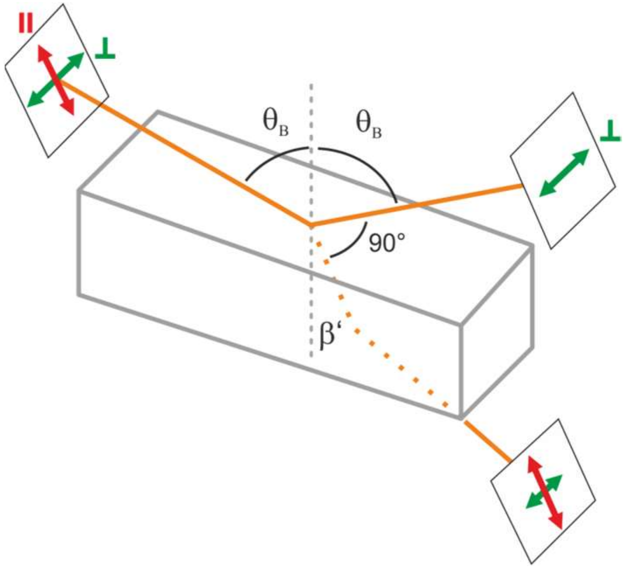


After reflection on mirror, components propagate in reversed order:

+x-component ahead of +y-component

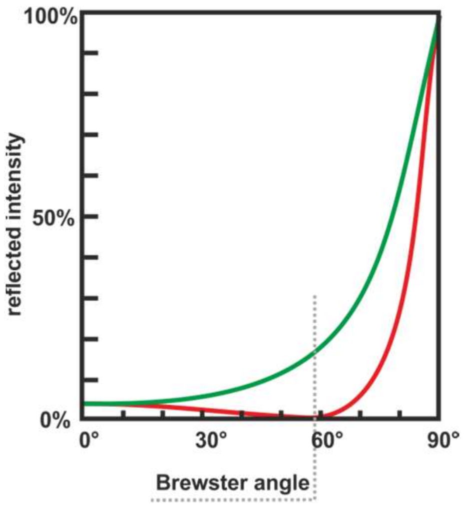
➢➢ Polarization inversion!

Polarized light and mirrors: Brewster angle



If angle of incidence $\alpha \neq 0°$, reflection coefficients are different for waves polarized parallel or perpendicular to plane of incidence.

- Circular polarization destroyed
- Intensity of linear polarized light angle dependent



- Intensity of reflected light depends on angle of incidence and refractive indices (Fresnel equations)
- Brewster angle, the angle at which reflected light only p-polarized:

$$\theta_B = \arctan\left(\frac{n_2}{n_1}\right)$$

A few terms commonly using in wave equations

period *T*: How long is a wave (in seconds)?

frequency *f*: How many waves/ periods per second? $f = \frac{1}{T} \quad [s^{-1}]$

velocity of a wave *c*: How fast is a wave? $c = \frac{\lambda}{T} = \lambda \cdot f \quad [m \cdot s^{-1}]$

Note: For EM waves, c = velocity of light

<u>The less catchy ones:</u>

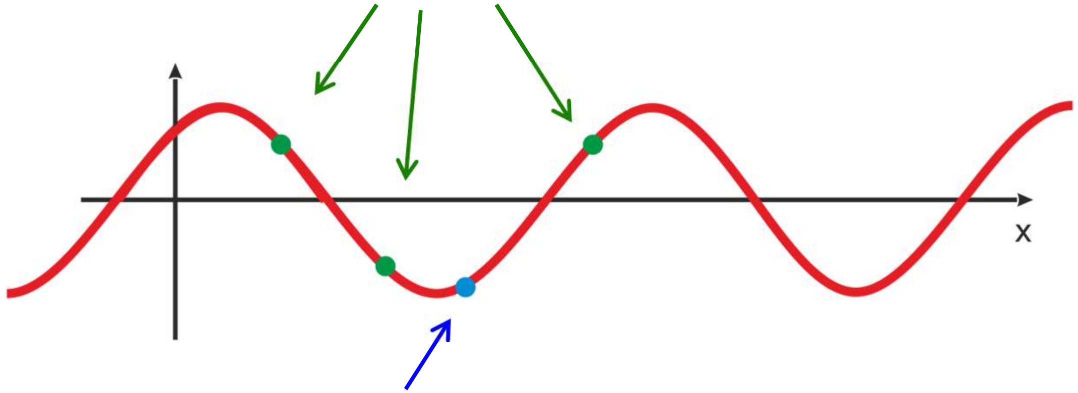
angular frequency ω: $\omega = \frac{2\pi}{T} = 2\pi \cdot f \quad [s^{-1}]$ kind of a frequency with respect to the number of full phases per unit time

wavevector $\vec{k}$: vector which stands perpendicularly on a wave,
usually pointing in the propagation direction of the wave

$\vec{k} = (k_x, k_y, k_z)$ and $|\vec{k}| = \frac{2\pi}{\lambda} = \frac{\omega}{c}$

Harmonic plane wave equation

(1) Watch this particle move (t=const): $A(x) = A_0 \cdot \cos(2\pi \frac{x}{\lambda} + \varphi_0)$



(2) Watch the amplitude at this position over time (x=const): $A(t) = A_0 \cdot \cos(2\pi \cdot \frac{t}{T} + \varphi_0)$

A combined, general equation is:

$$A(x,t) = A_0 \cdot \cos\left(\underbrace{2\pi \cdot f}_{=\omega} \cdot t - \underbrace{\frac{2\pi}{\lambda}}_{=k} x + \varphi_0\right) = A_0 \cdot \cos(\omega t - kx + \varphi_0)$$

Compensates simultaneous growth of x and t

Harmonic plane wave equation

Simplifying the trigonometric function
which now moves in z-direction

$$E_x = E_{0x} \cdot \cos(\omega t - kz + \varphi_0)$$

by using Euler‘s formula:

$$\cos(a) + i \cdot \sin(a) = e^{ia}$$

leads to:

$$E_x = E_{0x} \cdot \mathrm{Re}\left[e^{i(\omega \mathrm{t} - kz + \varphi_0)}\right]$$

… where „Re“ indicates that only the real part of the complex number is used.

Note: From now on, we drop the „Re“ but keep in mind that we only consider the real part of E_x.

Describing polarization states: Jones notation

Description of polarization state of perfectly polarized light in 2-component vector **J**, the so-called *Jones*-vector:

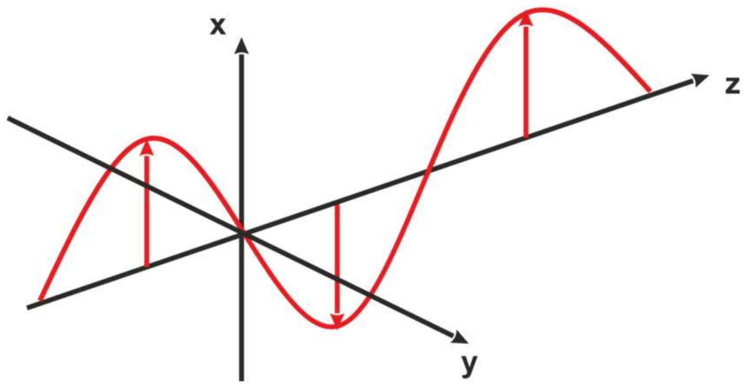
$$\mathbf{J} = \begin{pmatrix} E_x \\ E_y \end{pmatrix} \equiv \frac{1}{E} \cdot \begin{pmatrix} E_{0x} \cdot \mathrm{e}^{\mathrm{i}(\omega t - kz + \varphi_x)} \\ E_{0y} \cdot e^{\mathrm{i}(\omega t - kz + \varphi_y)} \end{pmatrix}$$

$$= \frac{1}{E} \begin{pmatrix} E_{0x} \cdot e^{i\varphi_x} \\ E_{0y} \cdot e^{i\varphi_y} \end{pmatrix} \cdot e^{\mathrm{i}(\omega t - \quad)}$$

with $\quad E_{0x}^2 + E_{0y}^2 = E^2(\cos^2 \omega t + \sin^2 \omega t) = E^2$

Therefore, the Jones vector is normalized and dimensionless.

Jones vectors: Examples for linear polarization

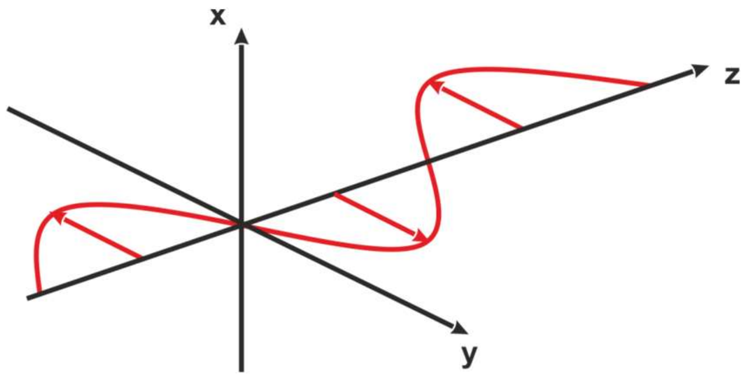


Linear polarized light in xz-plane
(0° polarized):

$$E_x = E_{0x} \cdot e^{i(\omega \mathrm{t} - k \qquad x)}$$
$$E_y = 0$$

$$\mathbf{J} = \frac{1}{\sqrt{E_{0x}^2 + 0^2}} \begin{pmatrix} E_{0x} \\ 0 \end{pmatrix} \cdot e^{i(\omega \mathrm{t} - kz + \varphi_x)}$$
$$= \begin{pmatrix} 1 \\ 0 \end{pmatrix} \cdot \underbrace{e^{i(\omega \mathrm{t} - kz + \varphi_x)}}_{}$$

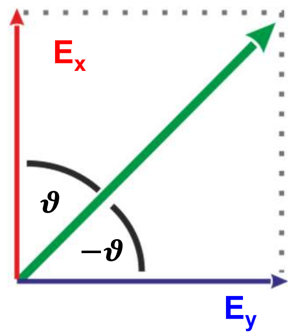
usually omitted
for simplicity



Linear polarized light in yz-plane
(90° polarized):

$$\mathbf{J} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

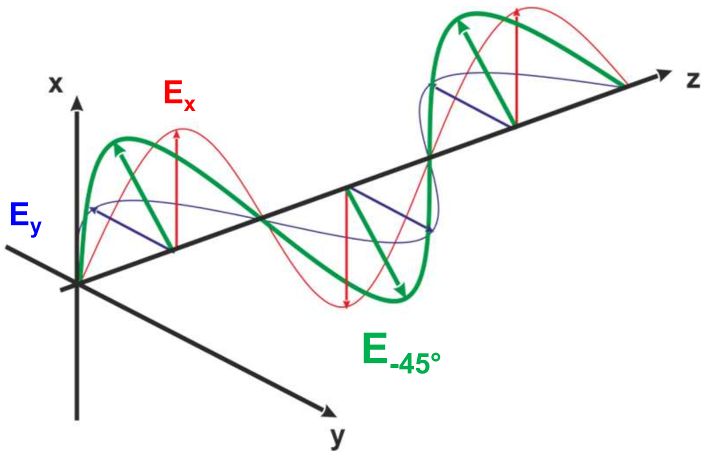
Jones vectors: Examples for linear polarization



For general angle of linear polarization
($\delta = \varphi_x - \varphi_y = 0$):

$$\frac{E_x}{E_\vartheta} = \cos(\vartheta) \rightarrow E_x = E_\vartheta \cdot \cos(\vartheta)$$

$$\frac{E_y}{E_\vartheta} = \cos(-\vartheta) \rightarrow E_y = E_\vartheta \cdot \cos(-\vartheta) = E_\vartheta \cdot \sin(\vartheta)$$



Insertion into the Jones vector definition:

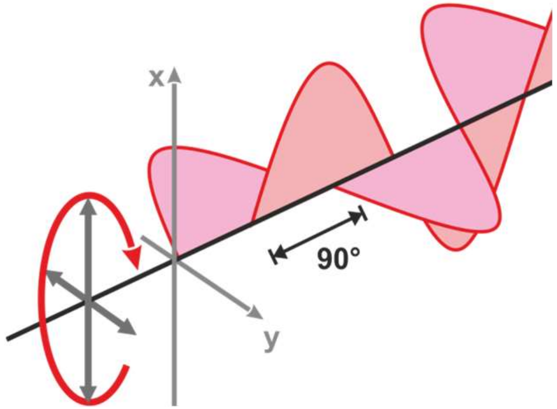
$$\mathbf{J} = \begin{pmatrix} E_x \\ E_y \end{pmatrix} = \frac{1}{\sqrt{E_\vartheta^2 \cos^2(\vartheta) + E_\vartheta^2 \sin^2(\vartheta)}} \begin{pmatrix} E_\vartheta \cdot \cos(\vartheta) \\ E_\vartheta \cdot \sin(\vartheta) \end{pmatrix}$$

$$= \begin{pmatrix} \cos(\vartheta) \\ \sin(\vartheta) \end{pmatrix}$$

.. which includes the special cases of 0° and 90° polarized light shown before.

Jones vectors: Examples for circular polarization

For right-circular polarization (observer's view):



$$\mathrm{E_{0x}} = \mathrm{E_{0y}} = \frac{\mathrm{E}}{\sqrt{2}}$$

$$\delta = \varphi_y - \varphi_x = -90° = -\frac{\pi}{2}$$

… i.e. y-component leads by 90° over x-component.

$$\mathbf{J_{RCP}} = \begin{pmatrix} E_x \\ E_y \end{pmatrix} = \frac{1}{E}\begin{pmatrix} E_{0x} \cdot e^{i\varphi_x} \\ E_{0y} \cdot e^{i\varphi_y} \end{pmatrix} = \frac{1}{E}\begin{pmatrix} E_{0x} \\ E_{0y} \cdot e^{i(\varphi_y - \varphi_x)} \end{pmatrix}$$

$$= \frac{1}{E}\begin{pmatrix} E/\sqrt{2} \\ E/\sqrt{2} \cdot e^{-i\frac{\pi}{2}} \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ e^{-i\frac{\pi}{2}} \end{pmatrix}$$

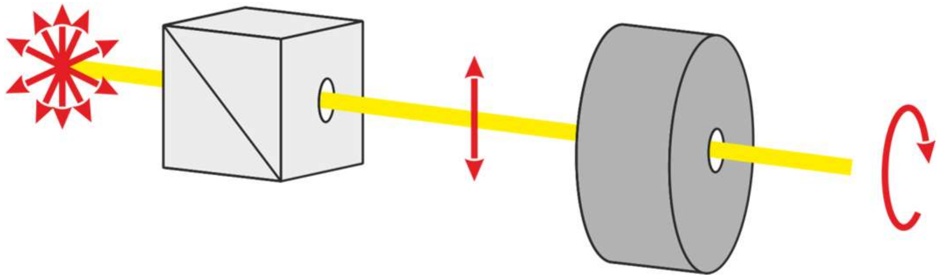
$$e^{-i\frac{\pi}{2}} = \cos\left(-\frac{\pi}{2}\right) + i \cdot sin\left(-\frac{\pi}{2}\right) = 0 + i \cdot (-1)$$

$$= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$$

$$\mathbf{J_{LCP}} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}$$

Working with Jones vectors

$$\begin{pmatrix}E_{0x}\\E_{0y}\end{pmatrix} \xrightarrow{LP_{45}} \begin{pmatrix}1\\0\end{pmatrix} \xrightarrow{\frac{\lambda}{4}} \begin{pmatrix}1\\-i\end{pmatrix}$$



Advantage:

- Polarization state is now described by simple 2-component vector
- Action of optical elements can be described with 2x2 matrix (multiplication from left)

$$\mathbf{I_{final}} = QWP \cdot LP_{45} \cdot I_0$$

Working with Jones vectors

Linear polarizer with axis of transmission parallel x $\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$

Linear polarizer with axis of transmission parallel y $\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$

Linear polarizer with axis of ±45° with x-axis $\frac{1}{2}\begin{pmatrix} 1 & \pm 1 \\ \pm 1 & 1 \end{pmatrix}$

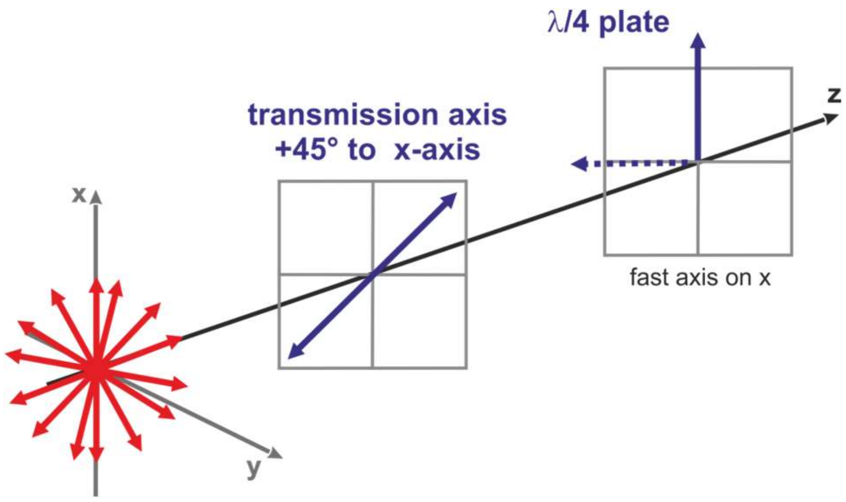
Right circular polarizer $\frac{1}{2}\begin{pmatrix} 1 & i \\ -i & 1 \end{pmatrix}$

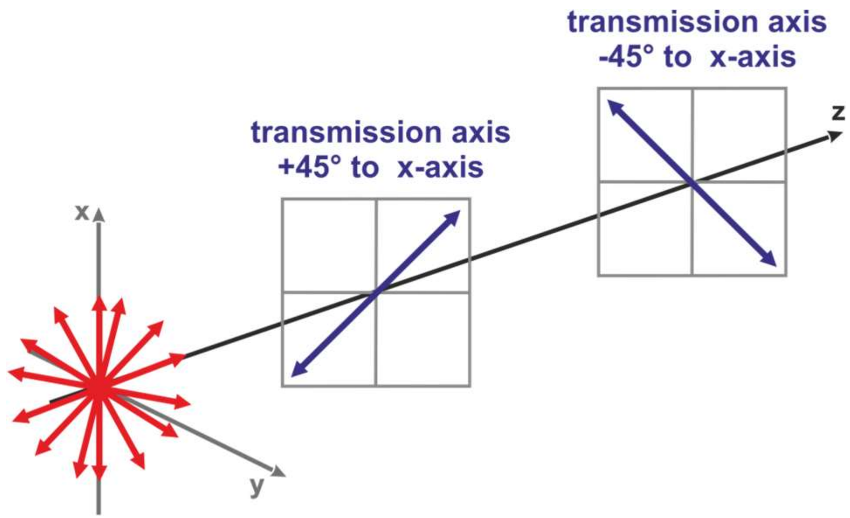
Left circular polarizer $\frac{1}{2}\begin{pmatrix} 1 & -i \\ i & 1 \end{pmatrix}$

Rotator $\begin{pmatrix} \cos\Theta & -\sin\Theta \\ \sin\Theta & \cos\Theta \end{pmatrix}$

Quarter wave plate with fast axis parallel x / y $e^{\frac{i\pi}{4}}\begin{pmatrix} 1 & 0 \\ 0 & i \end{pmatrix}$ $e^{\frac{i\pi}{4}}\begin{pmatrix} 1 & 0 \\ 0 & -i \end{pmatrix}$

Exercise: Calculating final polarization states





$$\boldsymbol{I_{LCP} = QWP_x \cdot LP_{+45} \cdot I_0}$$

$$\boldsymbol{= \begin{pmatrix} 1 & 0 \\ 0 & i \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} E_{0x} \\ E_{0y} \end{pmatrix} = \begin{pmatrix} 1+0 \\ 0+i \end{pmatrix}}$$

$$\boldsymbol{I_{CrossPol} = LP_{-45} \cdot LP_{+45} \cdot I_0}$$

$$\boldsymbol{= \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} E_{0x} \\ E_{0y} \end{pmatrix} = \begin{pmatrix} 1-1 \\ -1+1 \end{pmatrix}}$$

Partially polarized light: Müller matrices and Stokes vectors

$$\mathbf{S} = \begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{pmatrix} = \frac{1}{I_{total}} \begin{pmatrix} I_{total} \\ I_{45} - I_{135} \\ I_{RCP} - I_{LCP} \\ I_0 - I_{90} \end{pmatrix} = \frac{1}{E} \begin{pmatrix} E_{0x}^2 + E_{0y}^2 \\ 2E_{0x}E_{0y}\cos\delta \\ 2E_{0x}E_{0y}\sin\delta \\ E_{0x}^2 - E_{0y}^2 \end{pmatrix}$$

… with 4x4 matrices for optical elements, and a gigantic matrix for the sample which takes into account circular dichroism and linear dichroism as well as circular and linear birefringance:

$$\mathbf{SAMPLE}(\Theta)$$

$$= e^{-A} \begin{pmatrix} 1 + \frac{1}{2}(LD^2 + LD'^2) & -LD\sin 2\Theta - LD'\cos 2\Theta & CD + \frac{1}{2}(LD' \cdot LB - LD \cdot LB') & LD'\sin 2\Theta - LD\cos 2\Theta \\ -(LD\sin 2\Theta + LD'\cos 2\Theta) & \begin{array}{l} \left[1 + \frac{1}{2}(LD'^2 - LB^2)\right]\cos^2 2\Theta \\ \quad + \left[1 + \frac{1}{2}(LD^2 - LB'^2)\right]\sin^2 2\Theta \end{array} & LB'\sin 2\Theta - LB\cos 2\Theta & \begin{array}{l} -CB + \frac{1}{2}(LD^2 + LB^2 - LD'^2 - LB'^2)\sin 4\Theta \\ \quad + (LD \cdot LD' + LB \cdot LB')\cos 4\Theta \end{array} \\ CD + \frac{1}{2}(LD \cdot LB' - LB \cdot LD') & LB\cos 2\Theta - LB'\sin 2\Theta & 1 - \frac{1}{2}(LB^2 - LB'^2) & -(LB\sin 2\Theta + LB'\cos 2\Theta) \\ LD'\sin 2\Theta - LD\cos 2\Theta & \begin{array}{l} CB + \frac{1}{2}(LD^2 + LB^2 - LD'^2 - LB'^2)\sin 4\Theta \\ \quad + (LD \cdot LD' + LB \cdot LB')\cos 4\Theta \end{array} & LB'\cos 2\Theta - LB\sin 2\Theta & \begin{array}{l} 1 + \frac{1}{2}(LD'^2 - LB^2)\sin^2 2\Theta \\ \quad + \frac{1}{2}(LD^2 - LB'^2)\cos^2 2\Theta \\ \quad - 2(LD \cdot LD' + LB \cdot LB')\sin 4\Theta \end{array} \end{pmatrix} \tag{6}$$

Y. Shindo, *Opt. Eng.* **34** (1995) 3369

Outline of the lecture

	Dates	topics	
✓	Monday	Introduction	
✓		Polarization of light	
	Tuesday	Theoretical basis of optical activity	
		Optical rotation	
	Wednesday	Circular dichroism	
		Circular dichroism	
	Thursday	Vibrational optical activity	
		Vibrational optical activity	
	Oct 22?	applications	your part
	Oct 29?	applications	