Molecular Spectroscopy in Chemistry

prof. Oleg Boyarkin (3 3038, oleg.boiarkin@epfl.ch)

Schedule: every Friday,

16:15-18:00, room CH B331

Caldara Tiziano Agostino
Clerc Hugo André
Ding Zixuan
Fischer Thomas
Gaedecke Kelian Dietmar Marc
Hawkins Jasper Raymond
Huber Jan
Hügli Loïc
Jaccard Gladys Gwendoline Geneviève
Mikov Aleksandar Mihaylov
Nasturzio Pietro
Venancio Enzo Franck
Xie Qishan
Zupan Léa

13 lectures;
one session for solving problems;
oral exam.

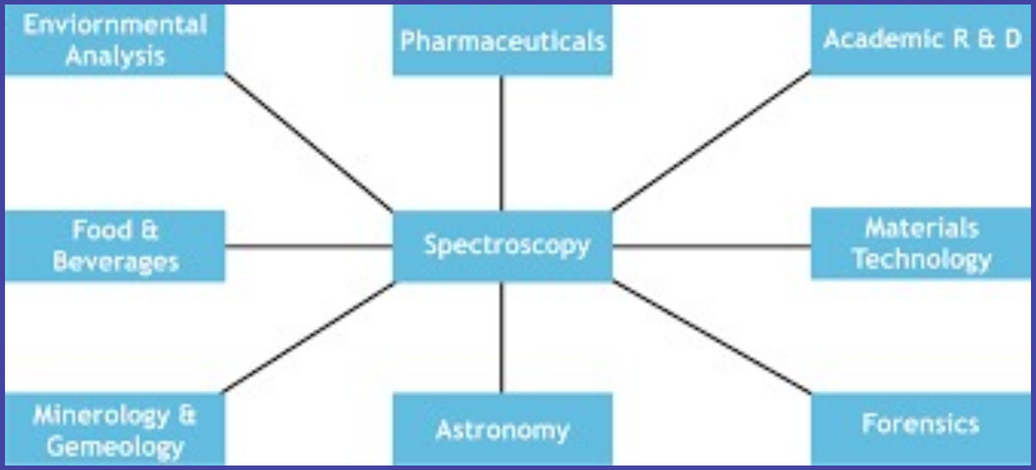
Online course PDF presentations in MOODLE (CH-456);

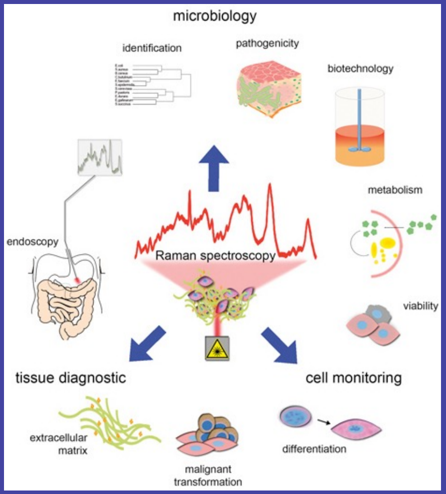
Course structure

- **Revision of basics**
  - Light as wave and particle
  - Quantum mechanics;
  - Spectroscopic transitions
- **Types of spectroscopy**
  - Absorption
  - Fluorescence
  - Raman
- **Analytical Spectroscopy in Chemistry**
  - Laser
  - FTIR
  - Raman microscopy
  - Photofragmentation
- **Selective chemistry and Laser isotope separation**
- **Spectroscopy in Astronomy (**Solar and exoplanets)

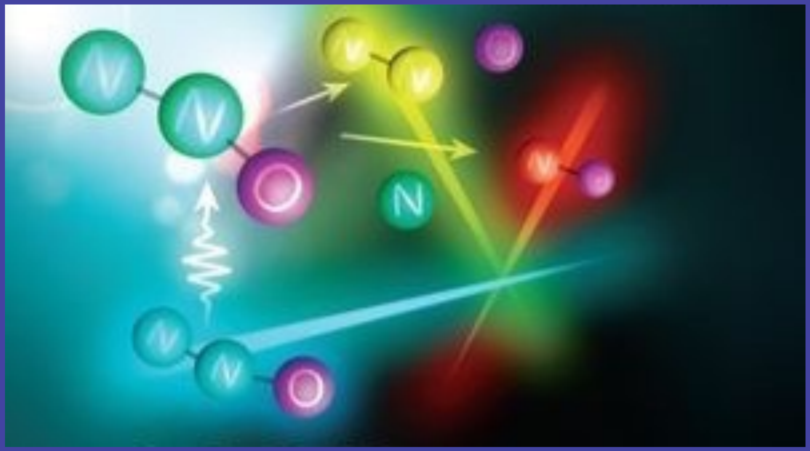
Spectroscopy in chemistry.

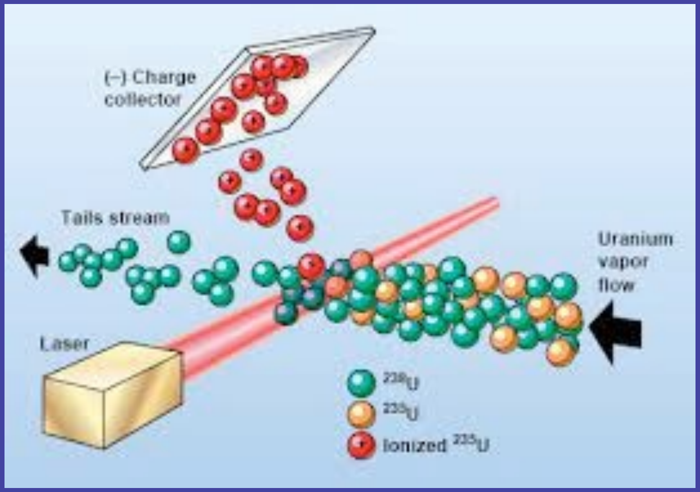
- *Analytical*: what, how much, where ?





- *Action*: light-driven selective chemistry

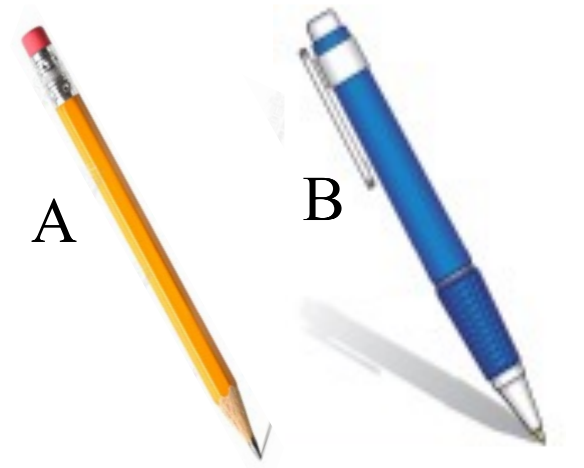




Concept of "library"

Which image is for a pen?

- *You have sets of visual properties in your memory for objects;*
- *You brain compares the images with these sets to identify them.*



Similar for molecules: one needs a set of physical observables to ***identify*** *a molecule: e.g., mass (MS), retention time (LC), chemical shifts (NMR),…*

For each technique these properties are to be measured (exceptionally computed) in advance for known standards and stored.

*This is called "**Library approach**"*

Spectroscopy identifies a molecule by its spectra: a result of interaction of light with molecules as a function of light wavelength.

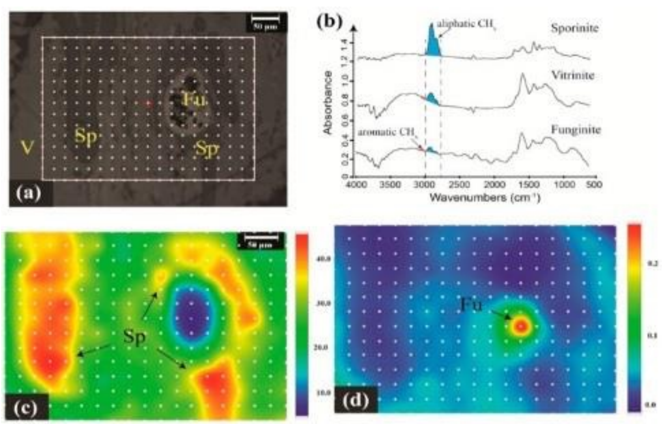
Quantification

Which box is larger?

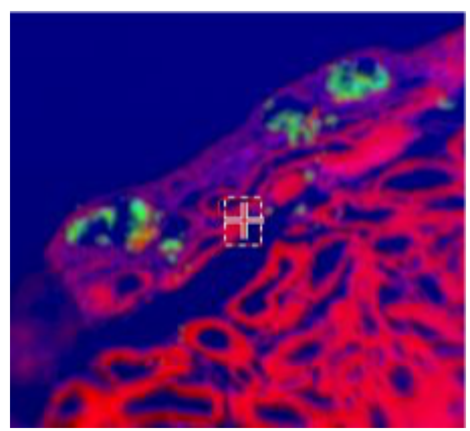
- *Need a **standard** to compare:*
e.g., attenuation of light by a sample relative to a standard of known concentration.

Location

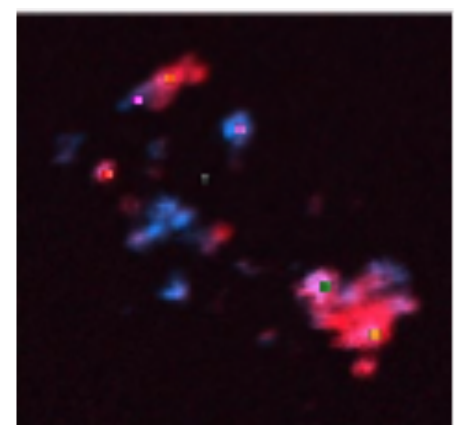
Light is to be directed to or light action is to be detected from a desired volume/surface only



Geological science



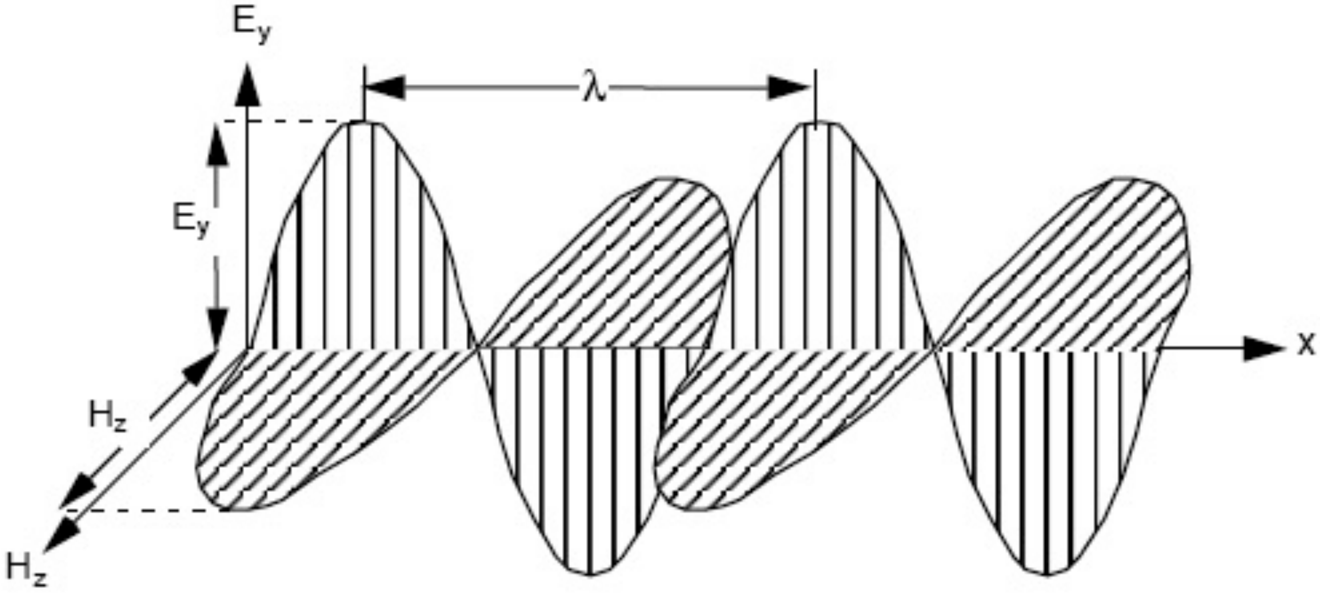
Cancer cells in tissue



Industrial defects

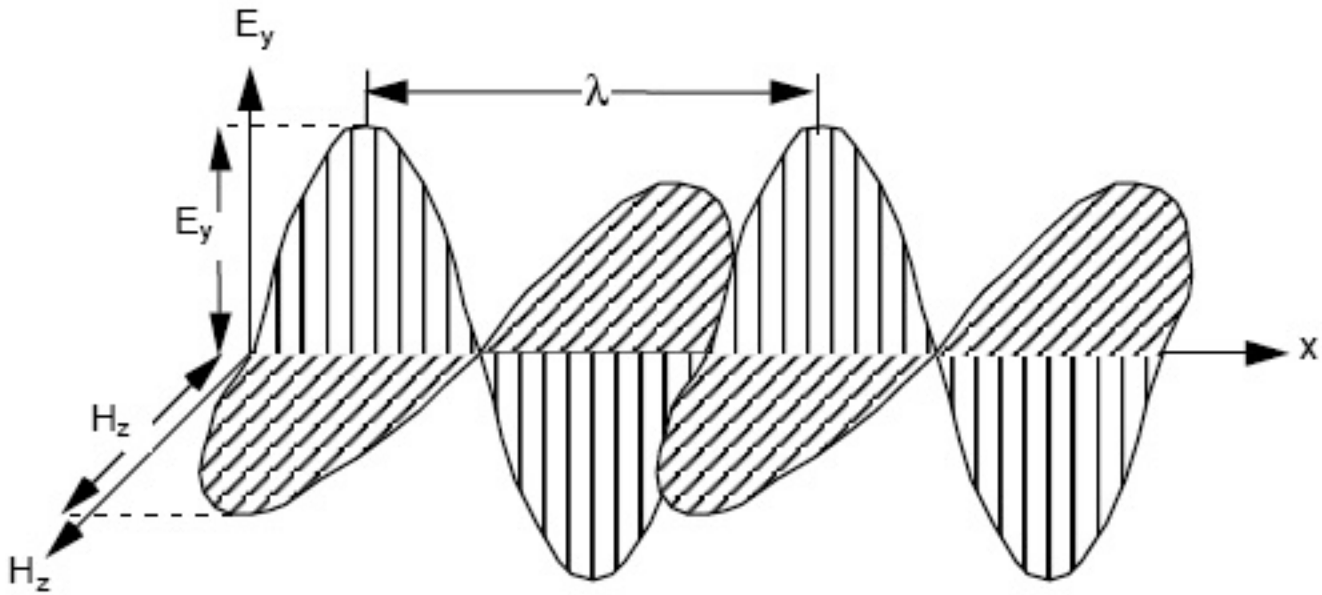
Review of fundamentals

Properties of Electromagnetic Radiation

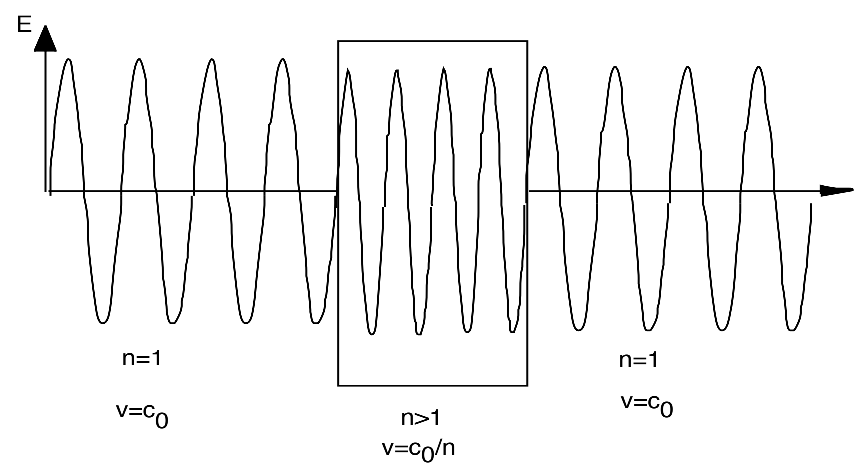


$$c = \lambda f \cong 3 \cdot 10^8 \text{ m/s} \qquad \lambda = \frac{c}{f}$$

Properties of Electromagnetic Radiation



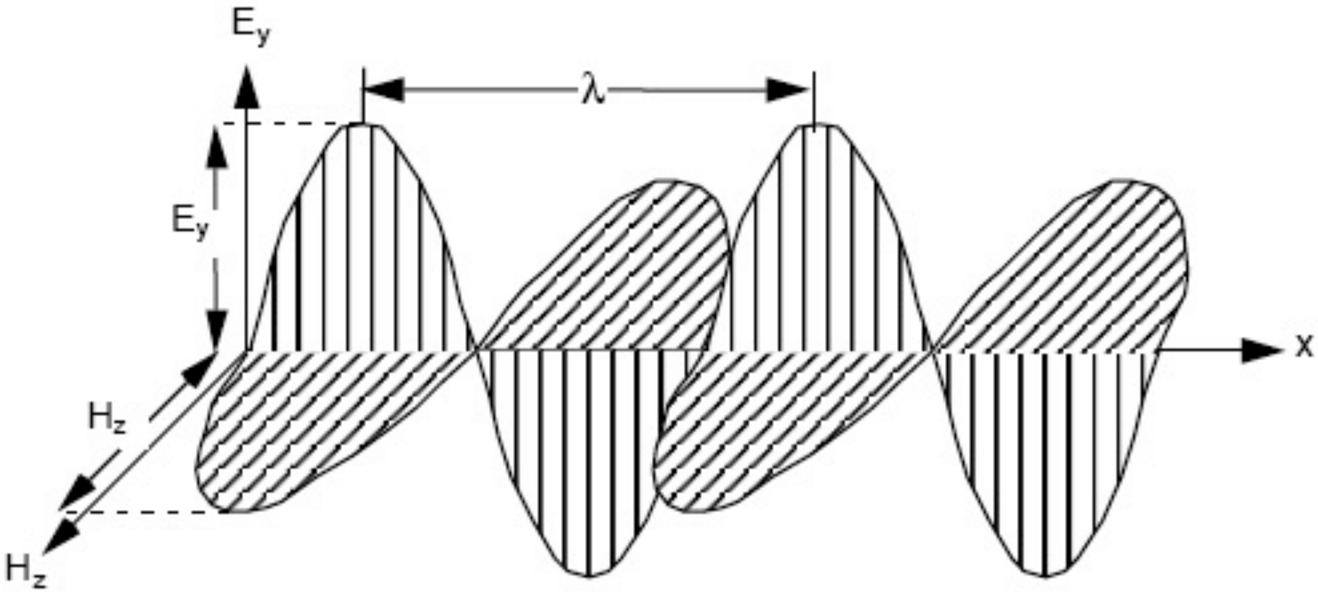
Refractive index of media $n = \dfrac{c}{V}$



$$\mathrm{v} = \frac{\mathrm{c}}{n} = \lambda_n \cdot f \qquad \lambda_n = \frac{\mathrm{c}}{n(f)\cdot f}$$

EMR propagates slower in any media, but with the same frequency

Properties of Electromagnetic Radiation



$$E(x,t) = E_{y0}\sin(2\pi ft + kx + \phi)$$

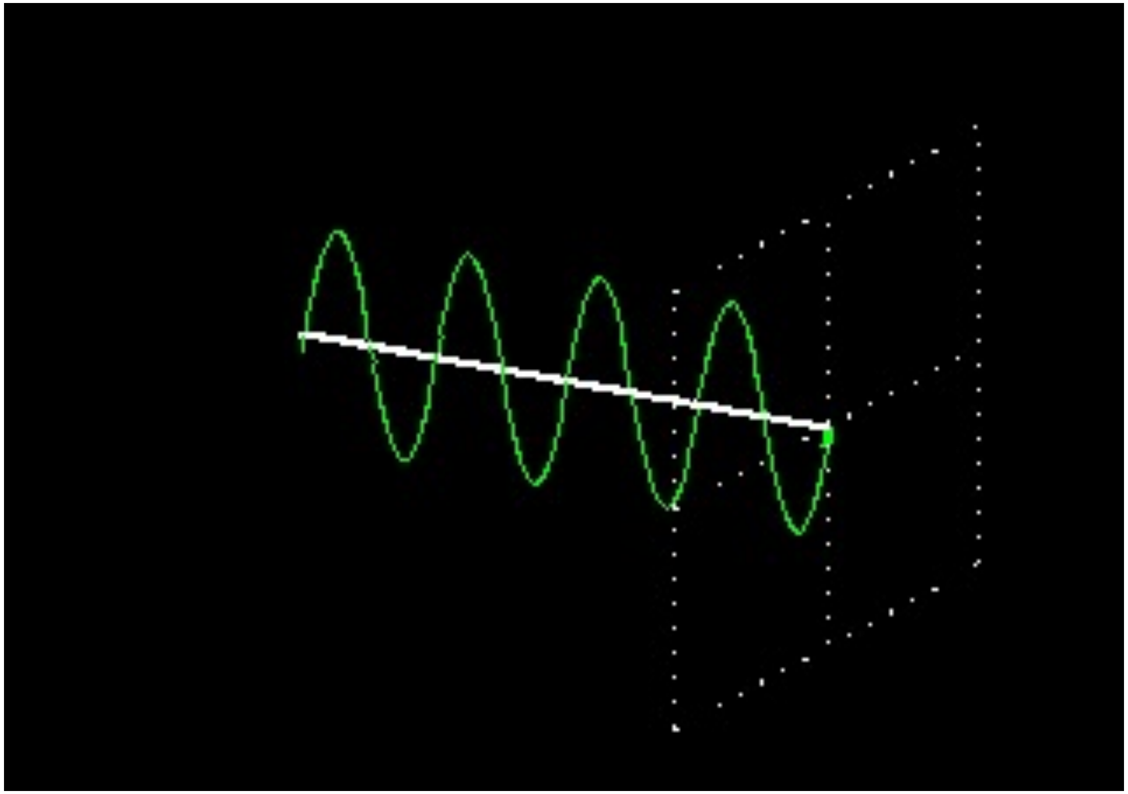
$$H(x,t) = H_{z0}\sin(2\pi ft + kx + \phi)$$

Wave vector: $|\vec{k}| = 2\pi/\lambda$ *(1/m)* ***Wave number:*** ***1/λ,*** *cm^{-1}*

Most of the observable effects are due to <u>electric</u> vector of EMW:

$$I = E_{yo}^2, \ (\mathrm{W/m^2})$$

Properties of Electric Waves



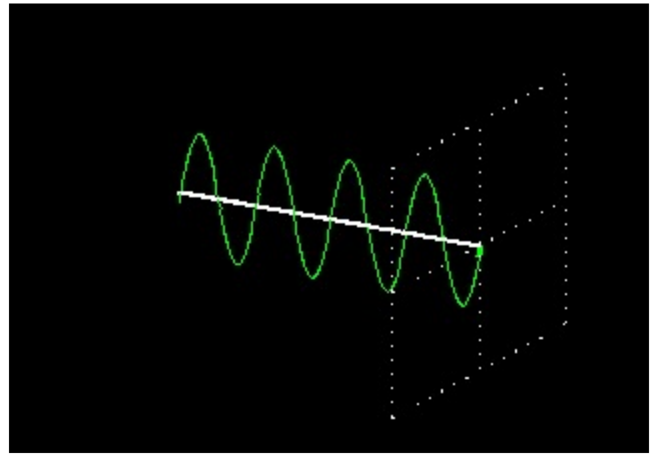
$$E(x,t) = E_{y0}\sin(2\pi ft + kx + \phi)$$

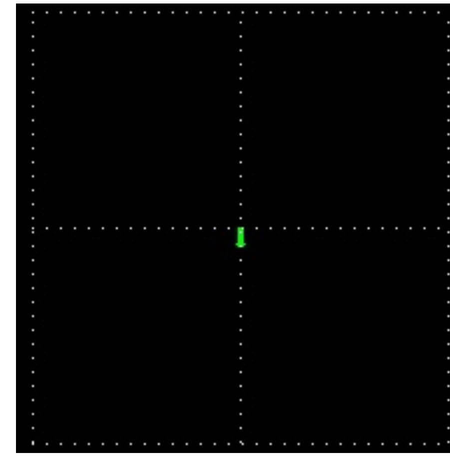
Linear/plane polarization

Plane-polarized electric wave

Vertically porarized

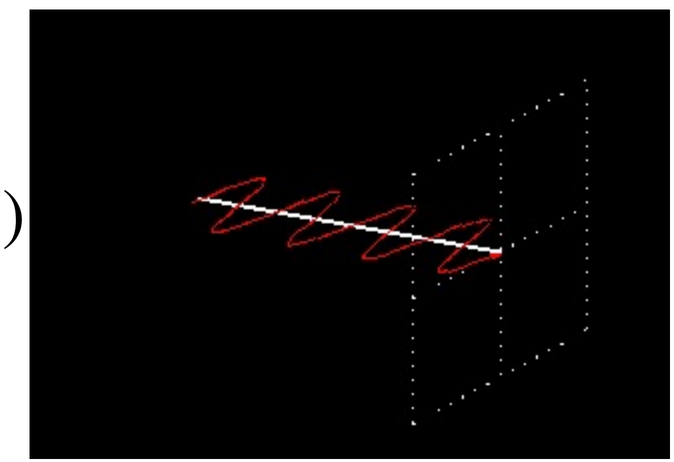
$$E_y(x,t) = E_{y0}\sin(2\pi ft + kx)$$

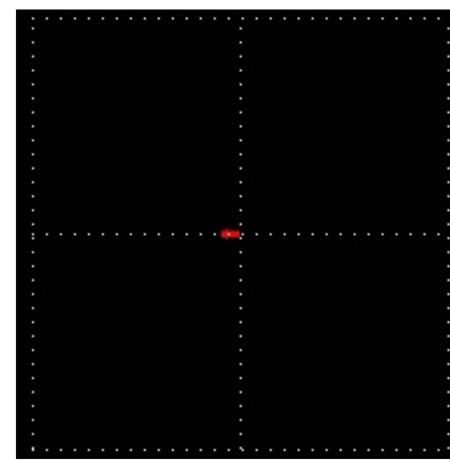




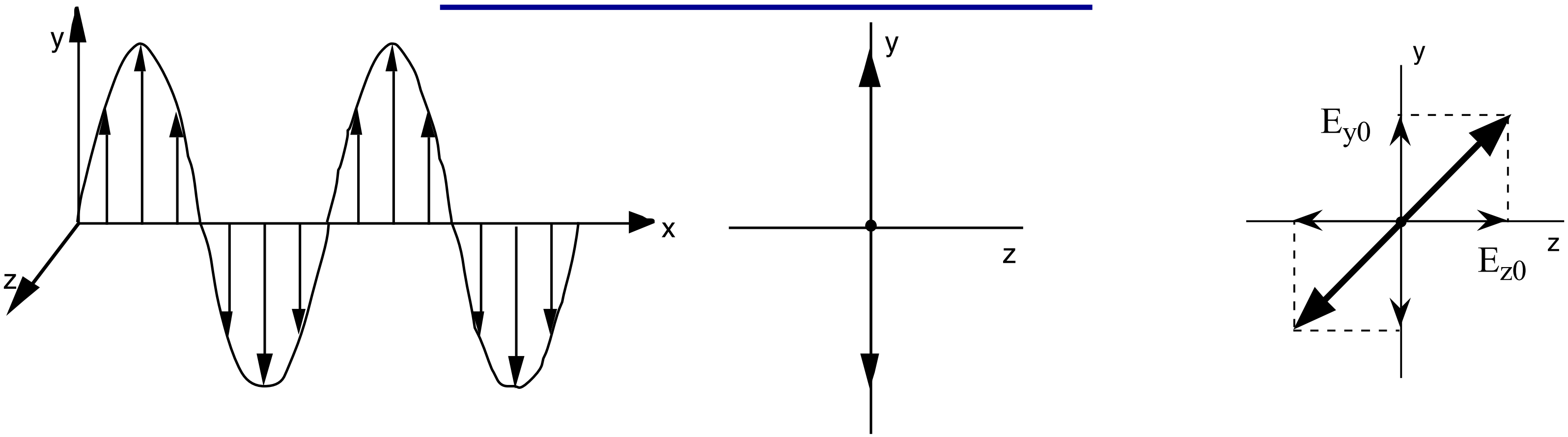
Horizontally polarized

$$E_z(x,t) = E_{z0}\sin(2\pi ft + kx)$$





POLARIZATION



$$\vec{E}(t,x) = \vec{E}_{y0}\sin(2\pi ft + kx + \phi_y) + \vec{E}_{z0}\sin(2\pi ft + kx + \phi_z)$$

What, if $E_{y0} = E_{y0}$ and $\delta = (\phi_y - \phi_z) = \pi/2 \pm n\pi$?

$$E^2 = E_0^2 \sin^2(2\pi ft + kx) + E_0^2 \sin^2(2\pi ft + kx + \pi/2)$$

$$E^2 = E_0^2[\sin^2(2\pi ft + kx) + \cos^2(2\pi ft + kx)] = E_0^2$$

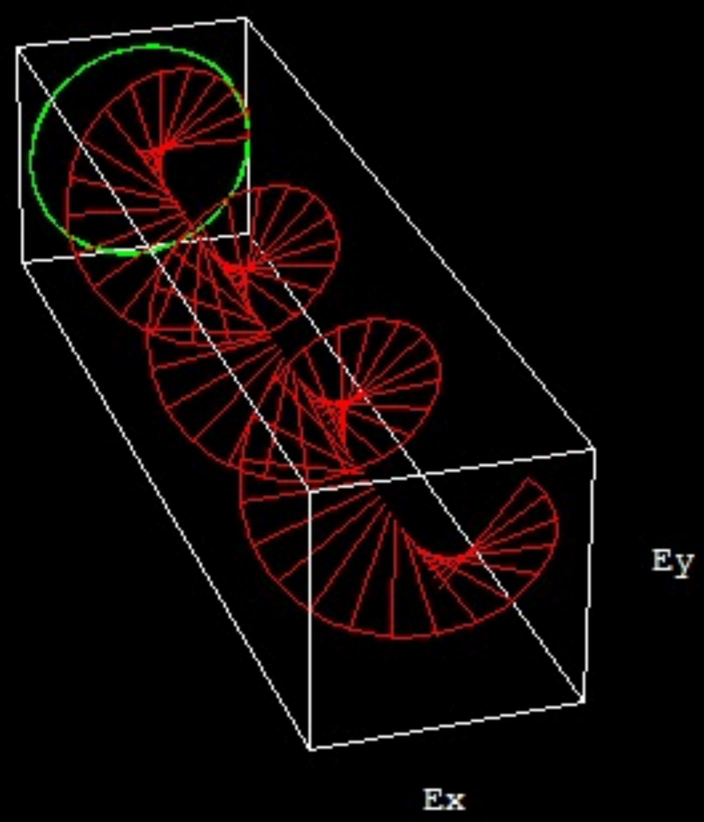
$E_0^2 = x^2 + y^2$ ***<= This is circle of radius E_0: Circular polarization***

Amplitude of electric vector is fixed

Tip of electric vector inscribes a circle

$\delta = \pi/2 \pm n\pi$

Circular polarization

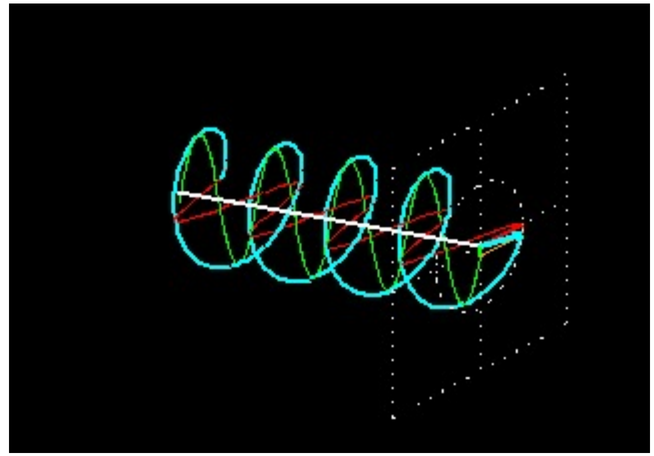


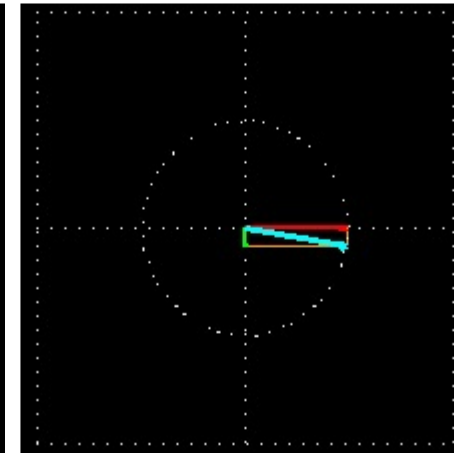
Circular polarized electric wave

Right circular

$$E_y(x,t) = E_{y0}\sin(2\pi ft + kx + 90°)$$

$$E_z(x,t) = E_{z0}\sin(2\pi ft + kx)$$

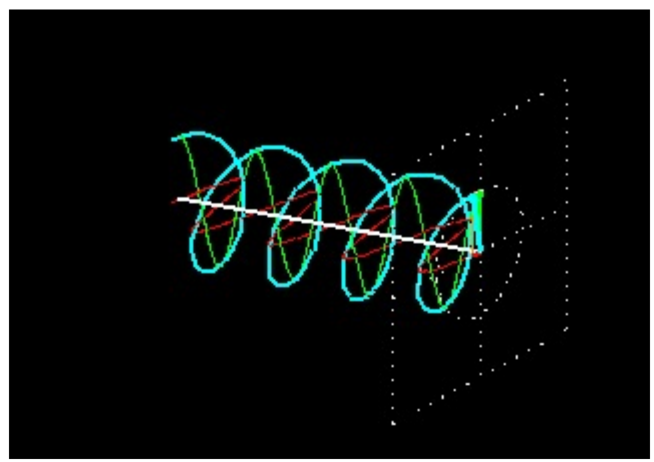


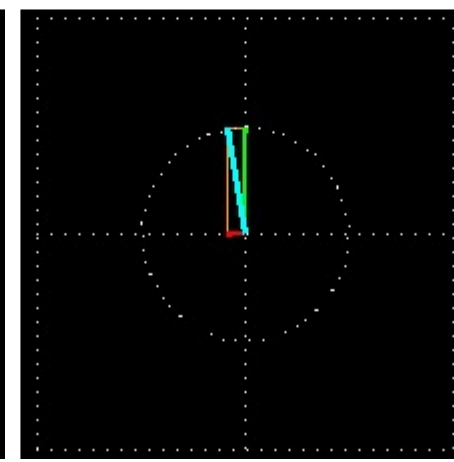


Left circular

$$E_y(x,t) = E_{y0}\sin(2\pi ft + kx - 90°)$$

$$E_z(x,t) = E_{z0}\sin(2\pi ft + kx)$$





Light dualism

Light is just a particular case of EMW with the wavelengths, which are much smaller than the size of the object our vision can resolve.

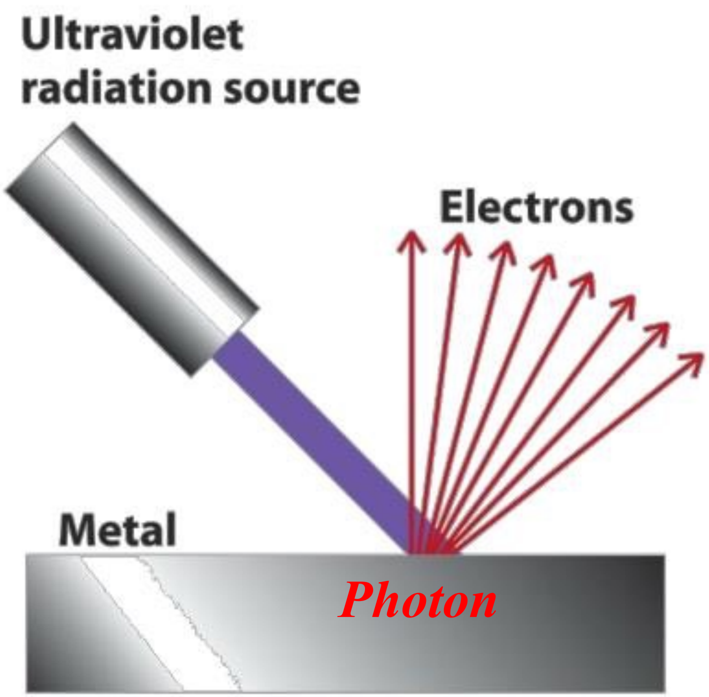
According to the Photo-Electric Effect: light behaves like particles

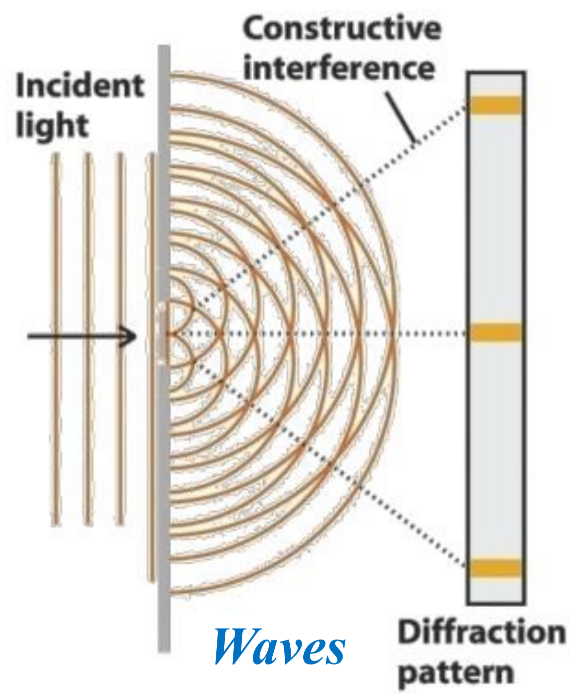
According to the 2-Slit Experiment: light behaves like waves

Interference of two waves

Modern concept of light:

Light has both wave-like and particle-like behavior





Properties of photon

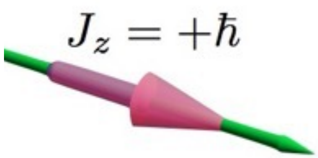
<u>*Photon energy:*</u> $E = h\nu$; $h = 6.626 \times$ 10-34 Joule·sec

Photon angular momentum (spin):

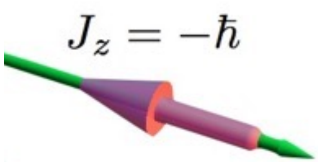
$J = \hbar = h/2\pi$; or in units of $\hbar$: $J=1$ =>

photons are *Bosons*.

$\vec{J}$ is a vector along the light propagation axis z:



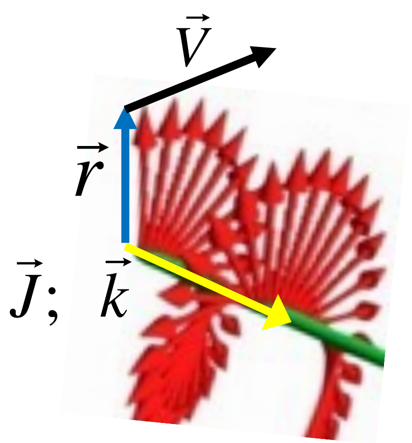
$J_z = \pm 1$ corresponds to the ***L***- and ***R***- polarized light.



Linear polarized light is a linear combination of ***L*** and ***R***.

$J_z \neq 0$, because photon is a massless particle that always moves with ***c***.

Classical picture: $\vec{E} \perp \vec{k}$, but $\vec{J} = \vec{V} \times \vec{r} \Rightarrow \vec{J} \parallel \vec{k}$



Properties of photon

Photon energy: $E = h\nu;$ h = 6.626 · 10^{-34} Joule·sec

Photon angular momentum (spin):

$J = \hbar = h/2\pi;$ (h is Plank's constant), or in units of $\hbar$: $J=1$ => photons are ***Bosons***. $\vec{J}$ is a vector along the light propagation axis z:

$J_z = \pm 1$ corresponds to the ***L***- and ***R***-polarized light.

Linear polarized light is a linear combination of ***L*** and ***R***.

Spectroscopic units:

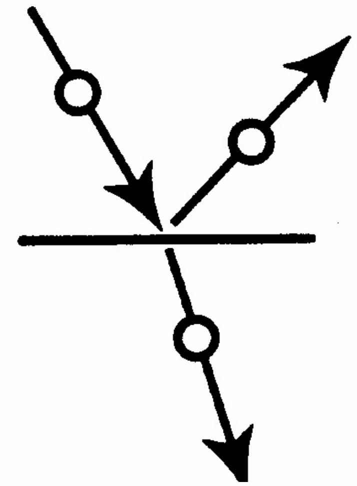
Frequency ν : sec^{-1} or Hz $E = h\nu;$

Wavelength λ : μm = 10^{-6}m or nm = 10^{-9} m or Å = 10^{-10}m $E = \dfrac{hc}{n \cdot \lambda_n}$

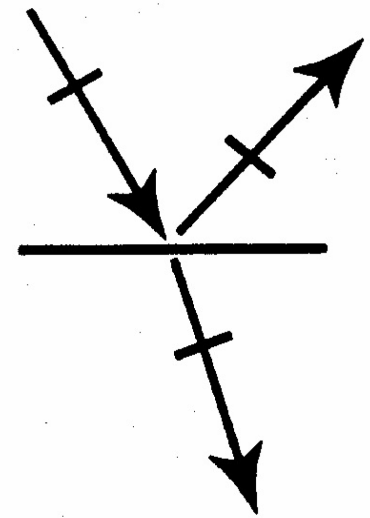
Wavenumber : $\tilde{\nu} \equiv 1/n\cdot\lambda_n = \dfrac{\nu}{c}$ cm^{-1} only! $E = \dfrac{hc}{n\lambda_n} = hc\tilde{\nu}$

Reflection of polarized light

Perpendicular ("**S**") polarization sticks up out of the plane of incidence.



Parallel ("**P**") polarization lies parallel to the plane of incidence.



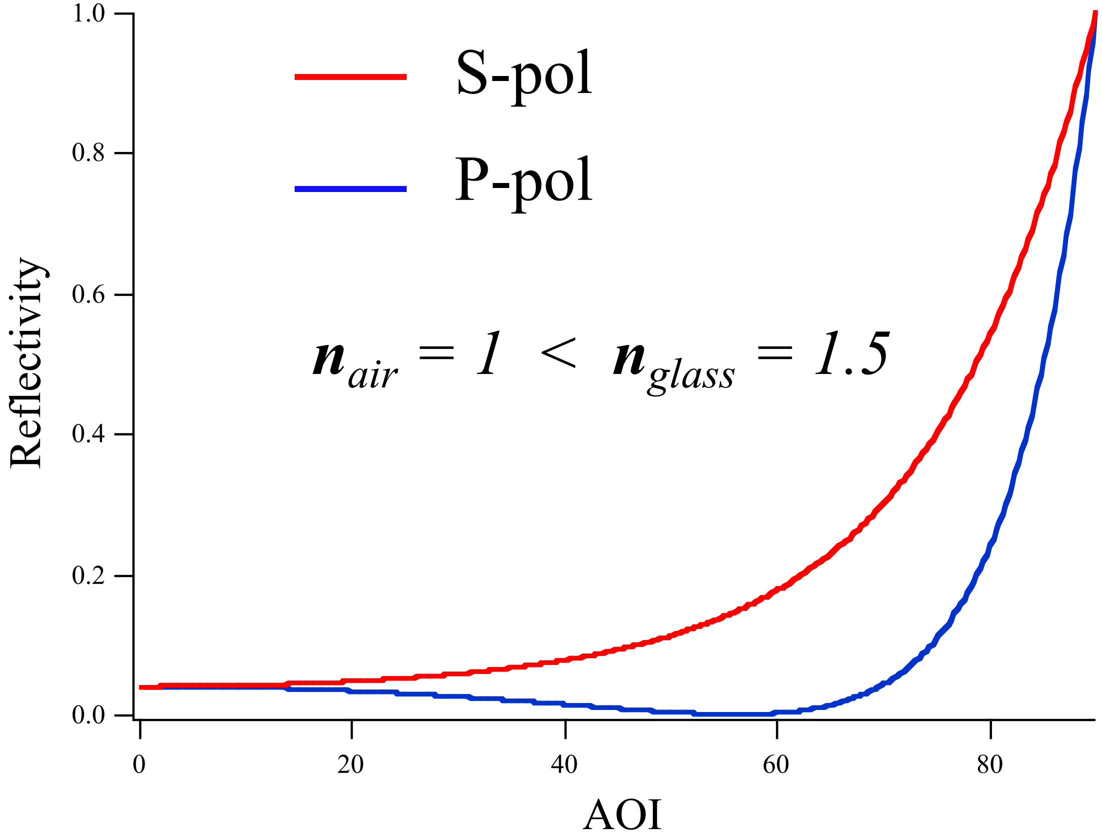
Does it matter for reflectivity ?

Reflection Coefficients for an Air-to-Glass Interface

Zero reflection for ***P*** polarization at **"Brewster's angle"** (56.3° here).

$$\tan\theta_{brewster} = \frac{n_t}{n_i}$$

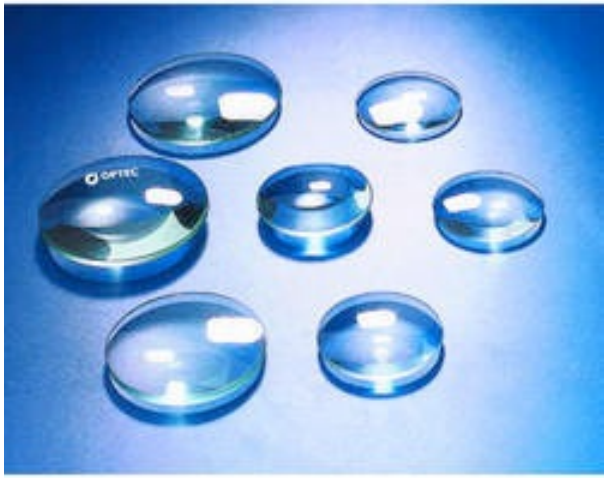
$$R(0) = \frac{(n-1)^2}{(n+1)^2}$$



Reflectivity 4% at normal incidence

Making image with thin lens

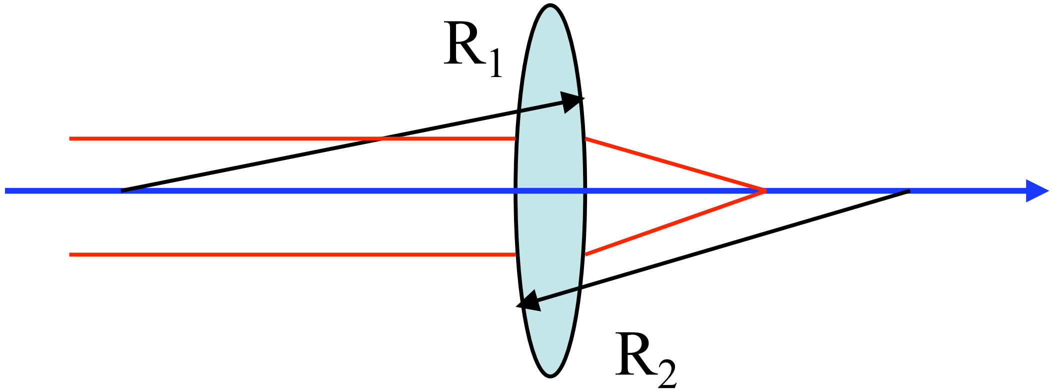
Lens is made of transparent material with n different from n of the media they are used in.



Glass, fused silica, plastic, ZnSe, Ge

They are optically polished (min scattering) with one or both sides curved (R_1, R_2); characterized by focal length f:

$$\frac{1}{f} = (n-1)\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$



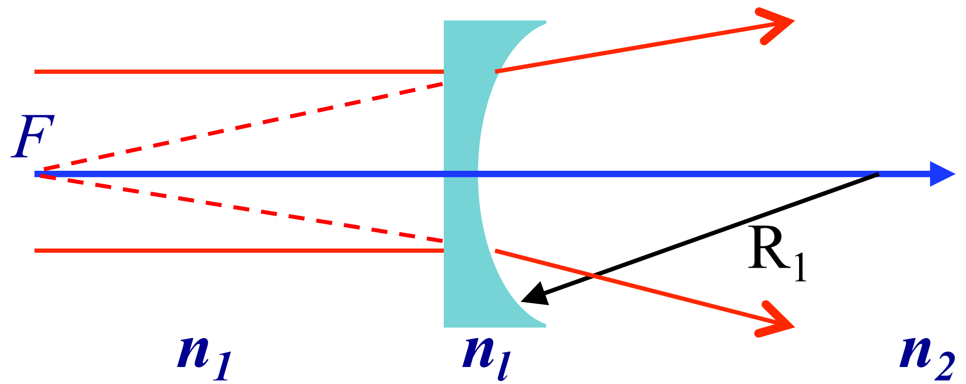
lens in air

BI-convex lens: $R_1 > 0$, $R_2 > 0$, => $f > 0$; positive

Making image with thin lens

They are optically polished (min scattering) with one or two sides curved (R_1, R_2); characterized by focal length f:

$$\frac{1}{f} = (n-1)\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$



lens in air

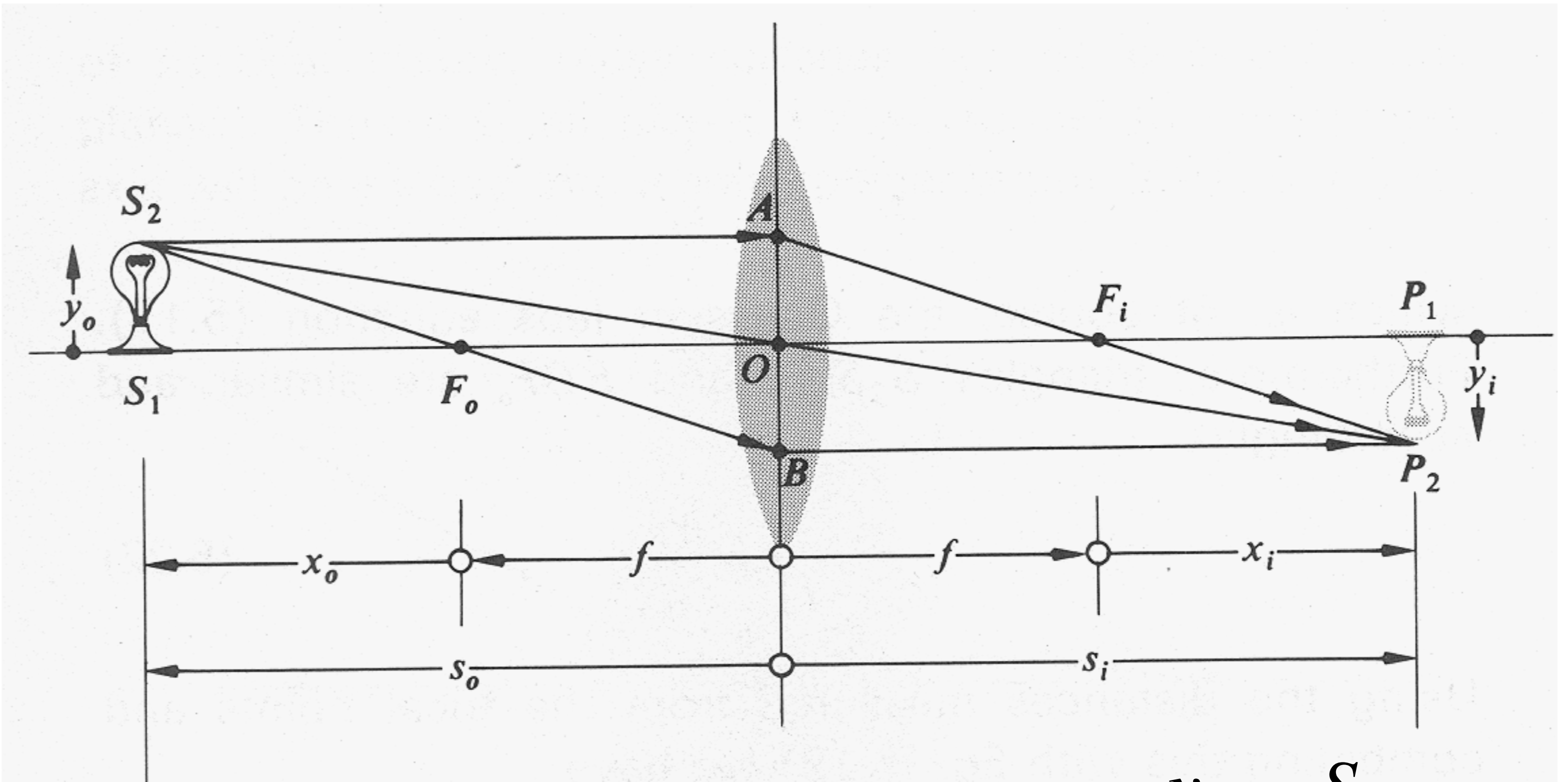
Plano-concave lens: $R_1 < 0$, $R_2 = \infty \Rightarrow f < 0$; negative

$$\frac{1}{f} = \frac{1}{s_o} - \frac{1}{s_i}$$

$f \leftrightarrow \infty;$

$2f \leftrightarrow 2f$

<u>*Lens imaging:*</u>



$S_0 > 0, \quad S_i < 0$

$$M = \frac{y_i}{y_o} = \frac{S_i}{S_o}$$

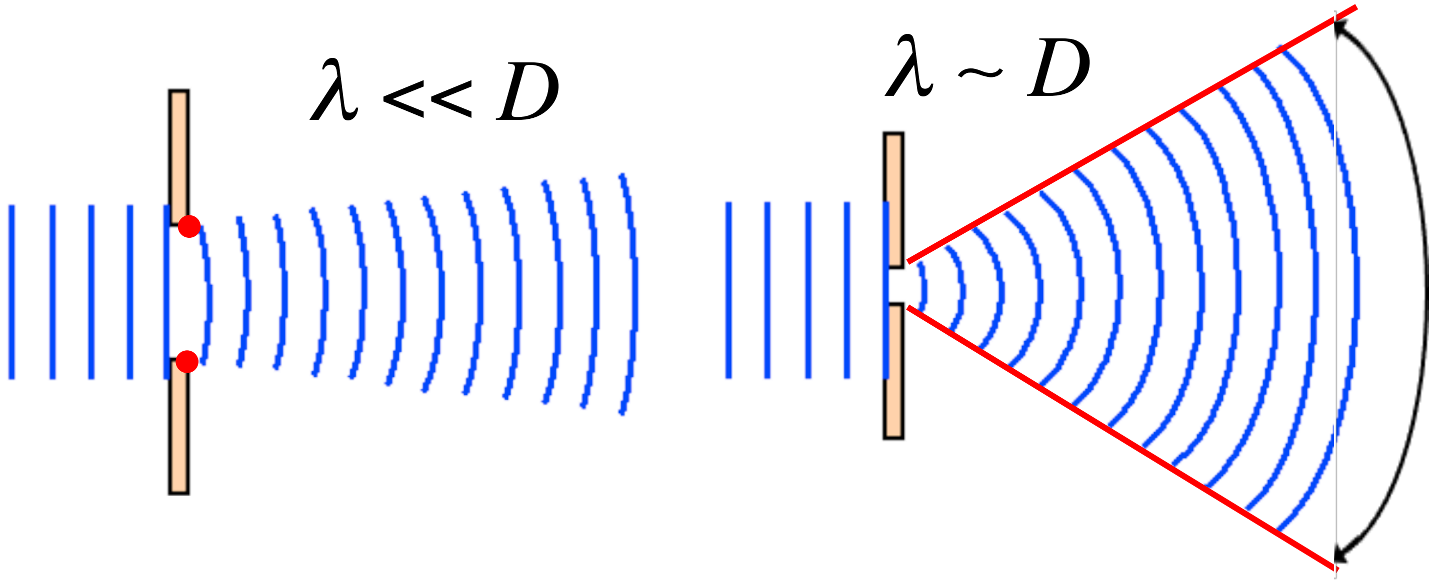
Name of Region	Wavelength Range	Wave number	Other Units
	3000 m		10^5 Hz
Radio Waves	{		
	0.3 m (30 cm)		10^9 Hz (1 GHz)
Microwaves (MW)	{		
	0.06 cm (600 μm)	16.6 cm^{-1}	
Far Infrared (FIR)	{		
	30 μm	333 cm^{-1}	
Mid Infrared	{		
	3 μm	3333 cm^{-1}	
Near Infrared (NIR)	{		
	0.8 μm (800 nm)	12,500 cm^{-1}	1.55 eV
Visible (VIS)	{		
	400 nm	25,000 cm^{-1}	3.1 eV
Ultraviolet (UV)	{		
	200 nm (2000 Å)	50,000 cm^{-1}	6.19 eV
Vacuum Ultraviolet (VUV)	{		
	100 nm (1000 Å)	100,000 cm^{-1}	12.4 eV
Extreme Ultraviolet (XUV)	{		
	5 nm (50 Å)		247.8 eV
x-rays and γ rays	{		
	10^{-3} Å		

Wave divergence

Wave expands (diverges) upon propagation and becomes larger than the entry.

$$\lambda \sim D$$

Diffraction on hole for $\lambda \approx D$



Divergence:

$$\theta_B = 2.44\frac{\lambda}{D}$$

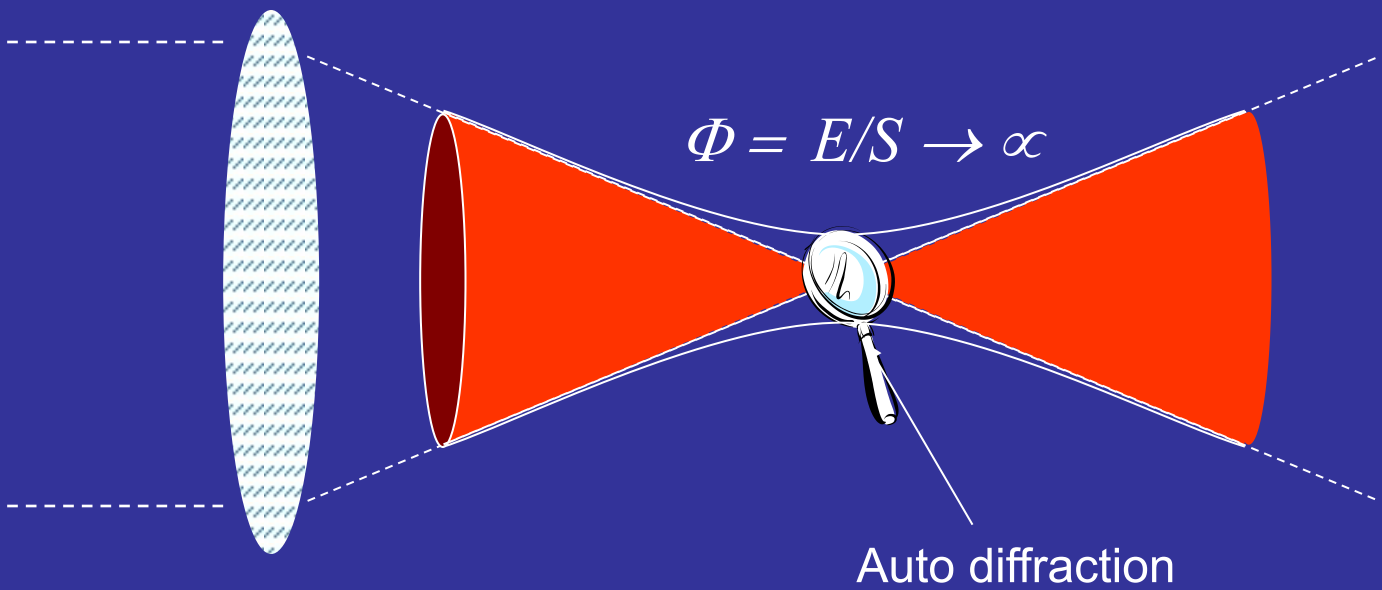
Any beam is divergent; at best, the divergence for a diffraction limited beam is

$$\theta = 2.44\frac{\lambda}{D}$$

Gaussian beams

Gaussian beams

What happens when we try to focus a laser beam?



The beam has a finite waiste size !

Gaussian beams

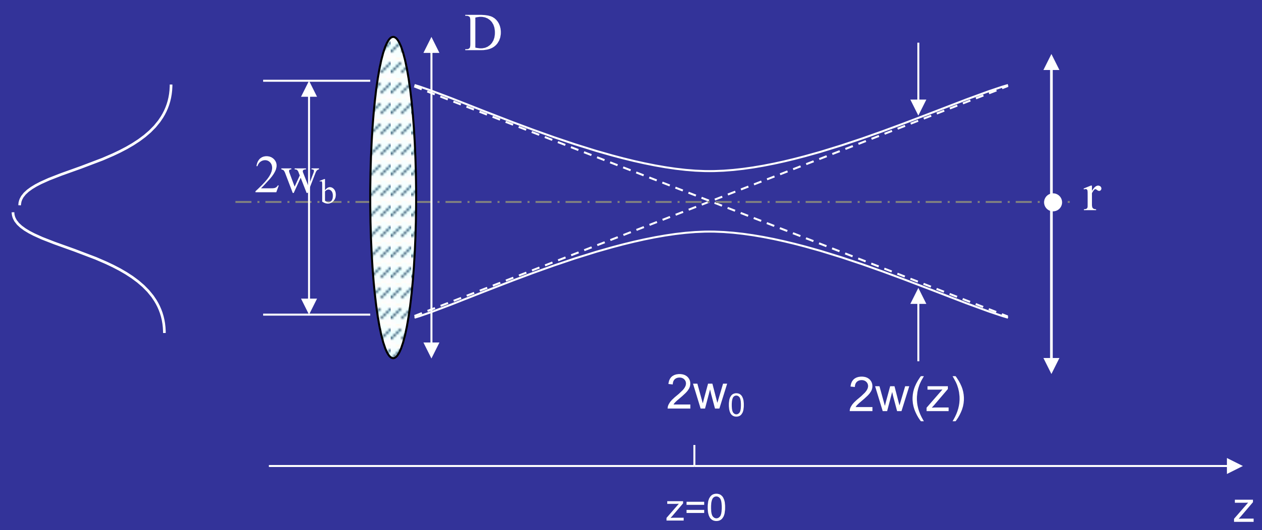
Hermite-Gaussian polynomials :

$$E_{mn}(x,y,z)=\frac{w_0}{w(z)}H_m\left(\frac{\sqrt{2}x}{w(z)}\right)H_n\left(\frac{\sqrt{2}y}{w(z)}\right)\exp\left[-\frac{r^2}{w^2(z)}-i\phi(r,z)\right]$$

Fundamental Gaussian beam (m=0, n=0):

Intensity:

$$I(r,z)=\frac{2P}{\pi w(z)^2}\exp\left(-2\frac{r^2}{w(z)^2}\right)$$

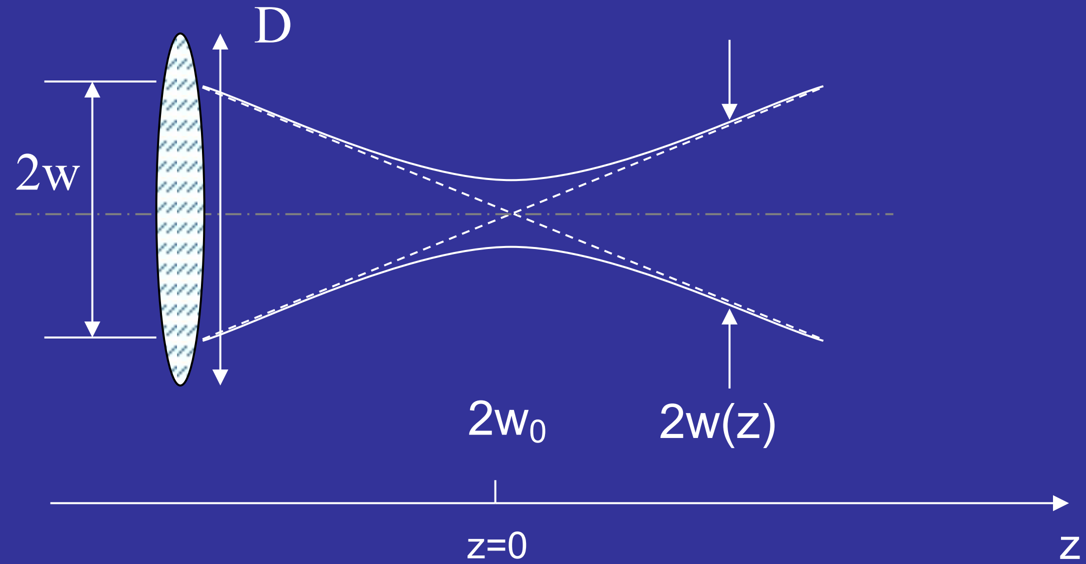


Fundamental Gaussian beam

Beam waist:

$(2w < D)$

$$2w_{\min} = 2.44\frac{\lambda \cdot F}{2w}$$



Beam waist:

$(2w \geq D)$

$$2w_0 = 2.44\frac{\lambda \cdot F}{D}$$

Divergence:

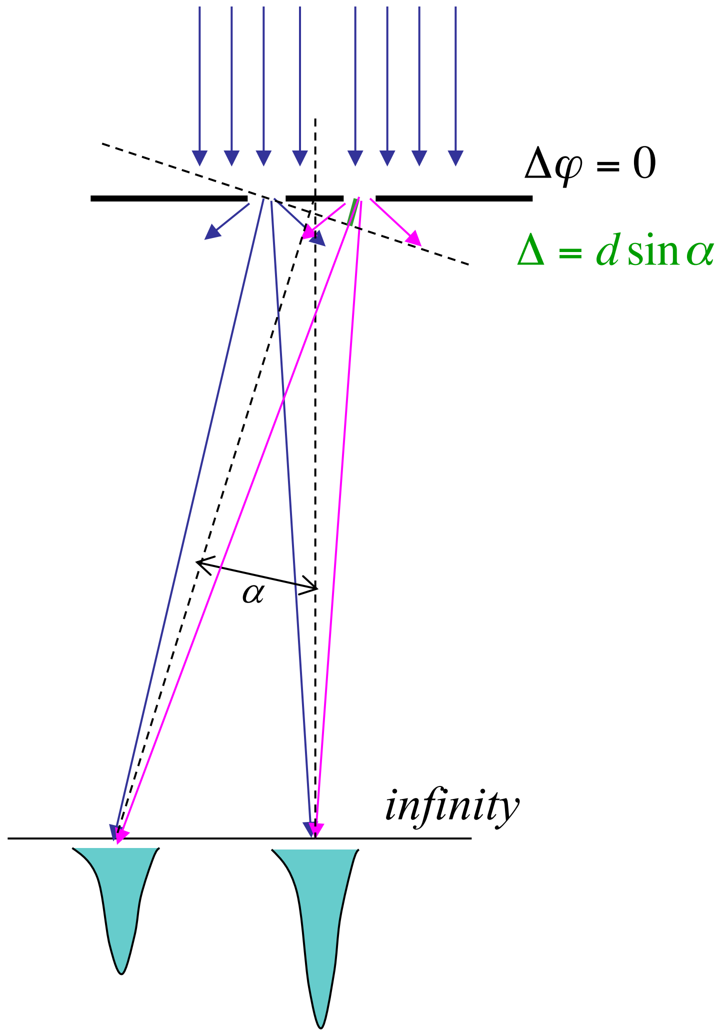
$$\theta_B = 2.44\frac{\lambda}{D}$$

$$2\omega_0 = \theta_B \cdot F$$

Interferometric Optics

- *Diffraction grating*
- *Interferometer Fabri-Perout*

Interference

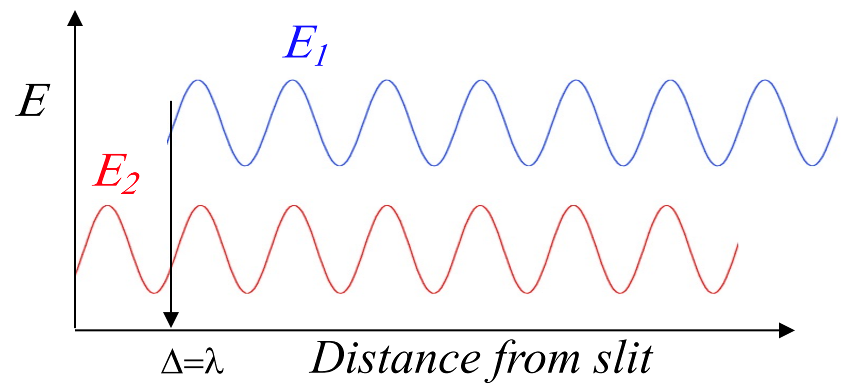


$$I = (\vec{E}_1 + \vec{E}_2)^2 = E_1^2 + E_2^2 + 2E_1E_2\cos(\varphi)$$

For max: $\varphi_{max} = 2\pi n$; $n = 0, 1, 2, \ldots$

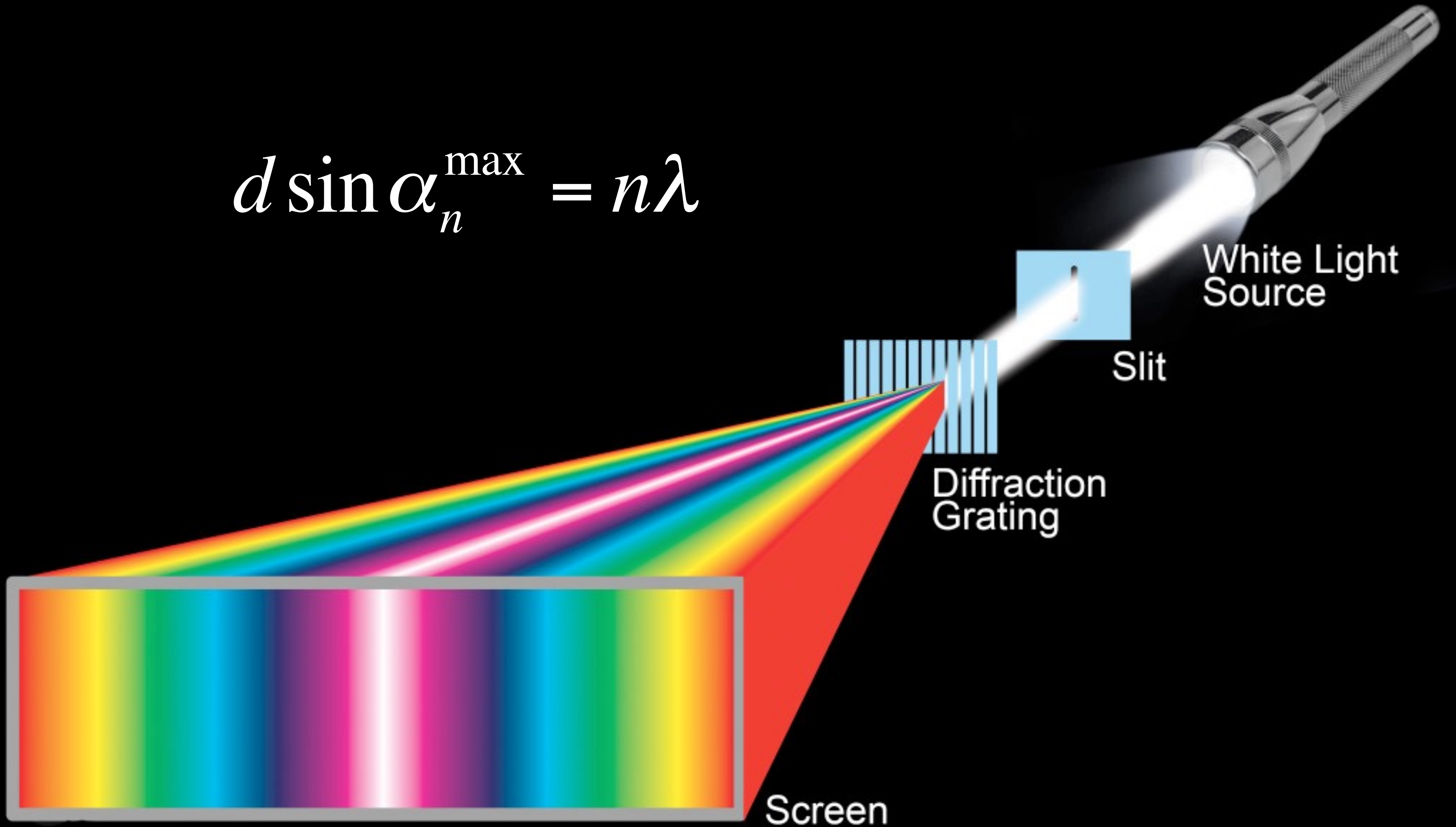
$$\varphi = 2\pi\frac{\Delta}{\lambda};$$

$$\Delta_{max} = n\lambda$$



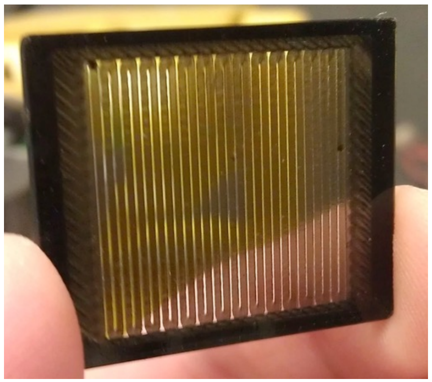
Multiple slit Interference

$$d \sin \alpha_n^{\max} = n\lambda$$



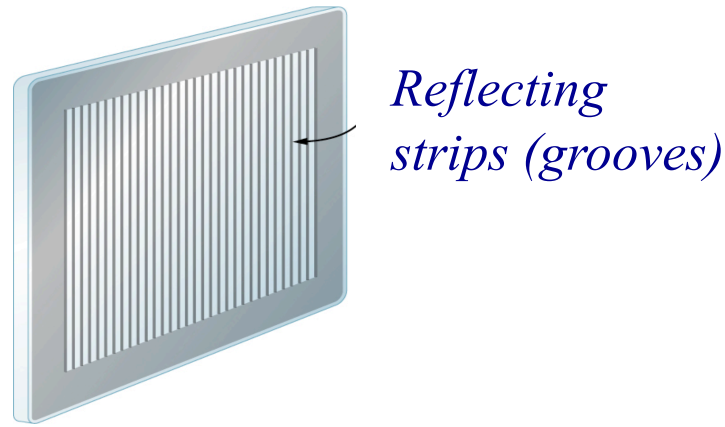
Diffraction grating

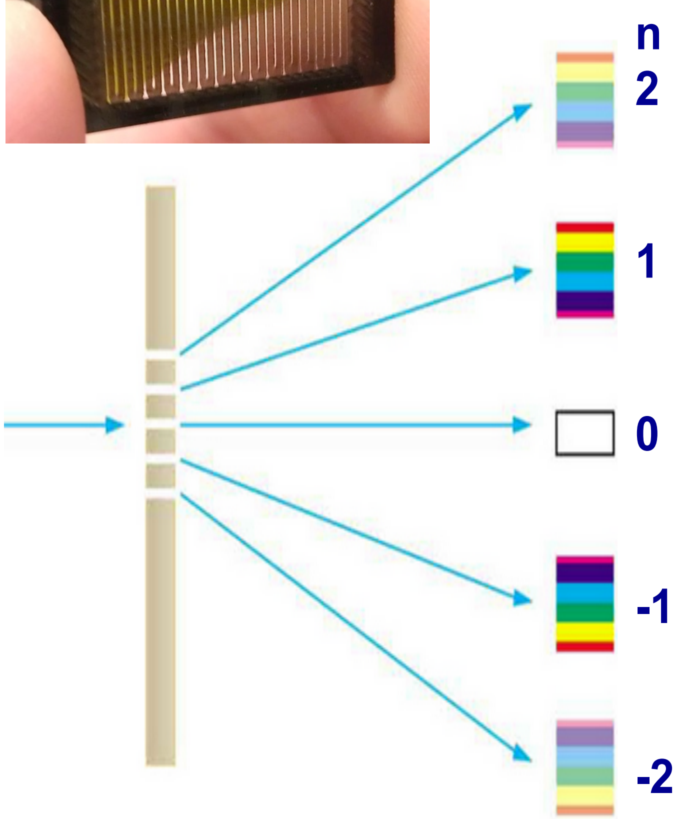
An optical device that disperses incoming rays of different wavelengths to different directions

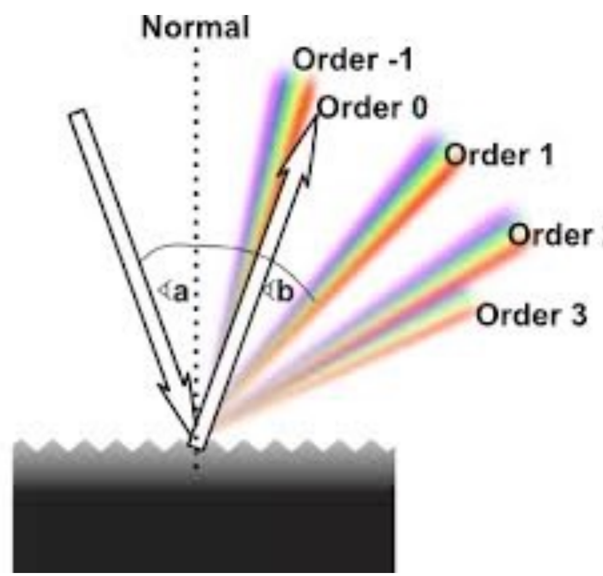


$$d\sin\alpha_n^{max} = n\lambda;$$

$$\lambda < d$$

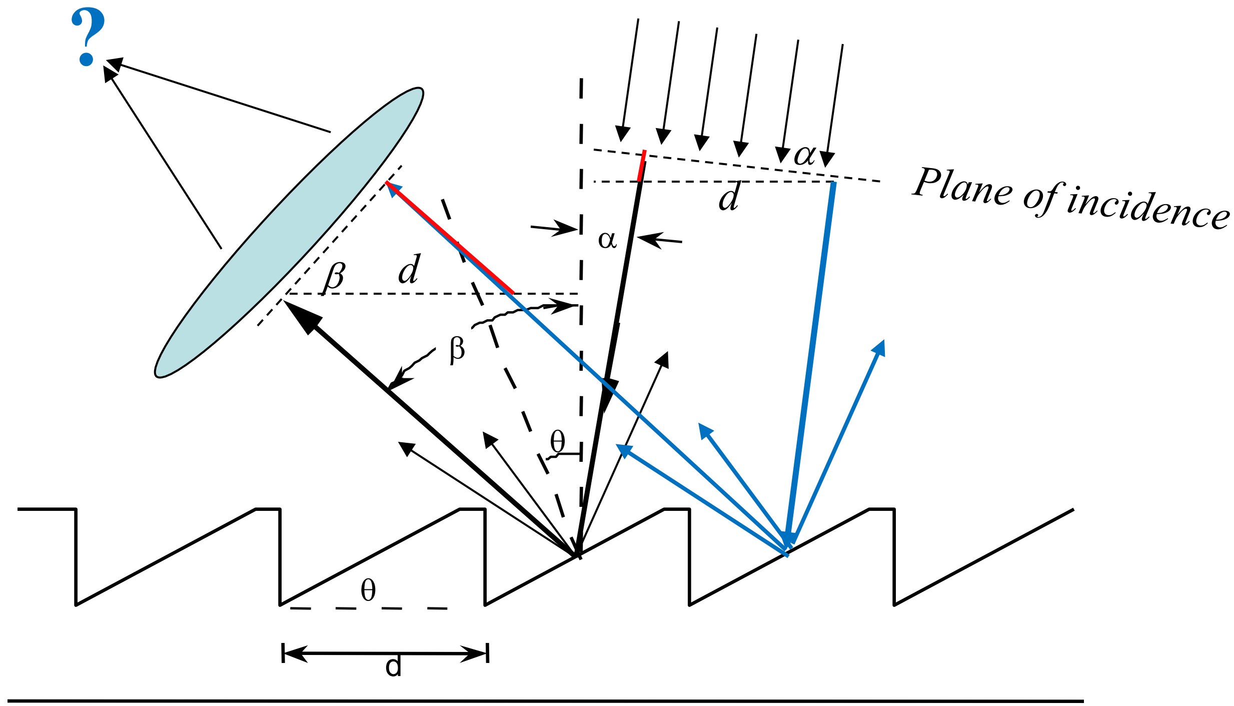






Interferometric Optics

Grating:



Path difference: $\Delta = d(\sin\alpha \pm \sin\beta)$

+ if α and β are on the same side;
– If α and β are on opposite sides

Phase difference: $$\varphi = 2\pi f \cdot \Delta t = 2\pi \frac{f\Delta}{c} = 2\pi \frac{\Delta}{\lambda}$$

$$\varphi = 2\pi \frac{d(\sin\alpha \pm \sin\beta)}{\lambda}$$

Grating

Electrical field by each ray: $E_n = E_1 \cos(n \cdot \varphi)$

Total electrical field:

$$E_{tot} = \sum E_1 \{1 + \cos\varphi + \cos 2\cdot\varphi + \ldots + \cos N\cdot\varphi)\}$$

Total intensity: $I_{tot} = \left| E_{tot} \right|^2$

Complex function presentation

1. Euler formula:

$$e^{i\vartheta} = \cos\vartheta + i\sin\vartheta \;\Rightarrow \mathrm{Re}(e^{i\vartheta}) = \cos\vartheta$$

$$E_n = E_1(\cos n\varphi) = E_1 \,\mathrm{Re}(e^{in\varphi})$$

Grating

Total amplitude:

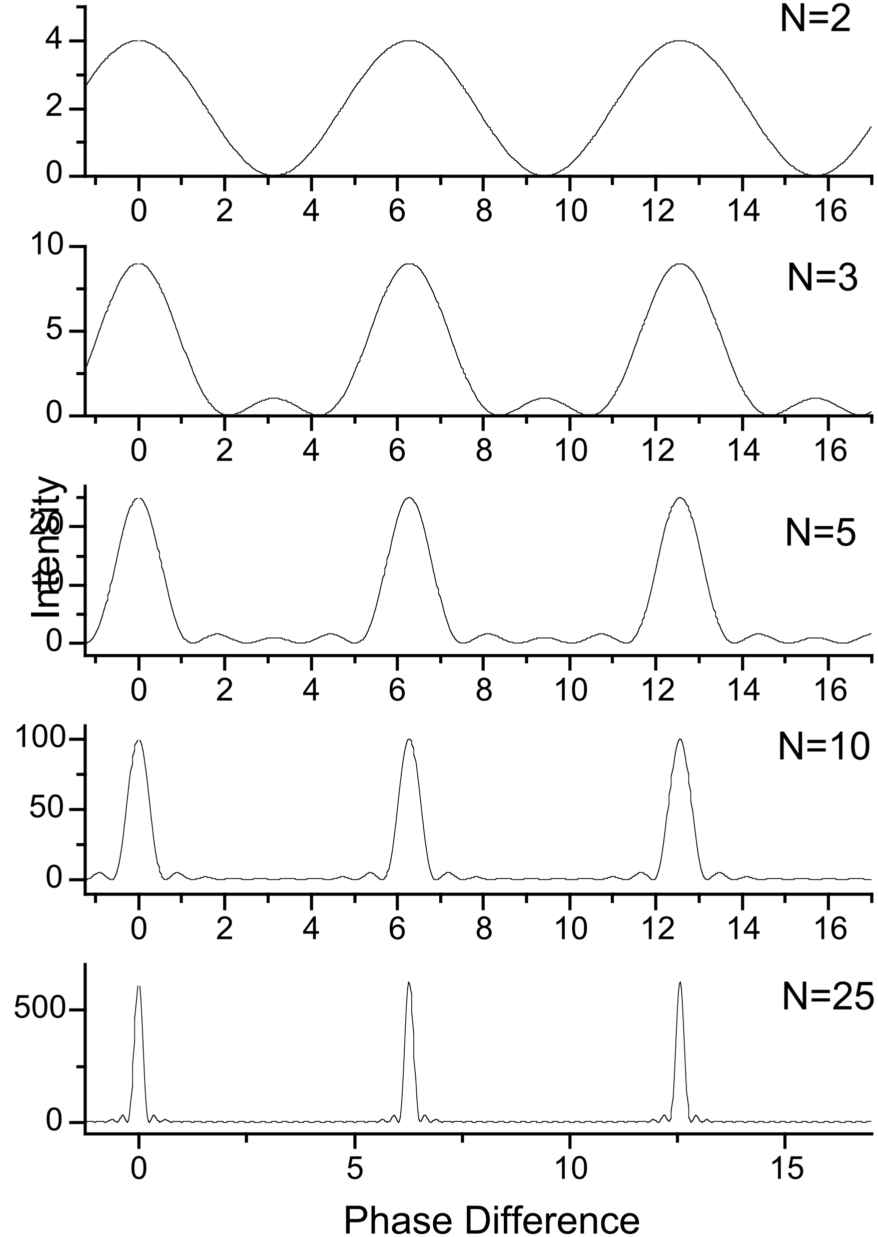
$$E_{tot} = E_1 (1 + e^{i\phi} + e^{i2\phi} + e^{i3\phi} + \ldots + e^{iN\phi})$$

$$E_{tot} = E_1 (1 + e^{i\phi} + e^{i2\phi} + e^{i3\phi} + \ldots + e^{iN\phi}) = E_1 \frac{1 - e^{iN\phi}}{1 - e^{i\phi}}$$

Total intensity:

$$I_{tot} = \left| E_{tot} \right|^2 = E_0^2 \frac{1 - \cos N\varphi}{1 - \cos\varphi} = I_0 \frac{\sin^2(N\varphi / 2)}{\sin^2(\varphi / 2)} \simeq I_0 N^2$$

Total intensity:



$$I_{tot} = I_0 \frac{\sin^2(N\varphi/2)}{\sin^2(\varphi/2)} \rightarrow I_0 \cdot N^2; \text{ for } (\varphi/2 \rightarrow 0 + n\pi);$$

Maximum intensity:

$$\varphi / 2 = 0, \pi, 2\pi, 3\pi, \ldots m\pi$$

$$\varphi = 2\pi \frac{d(\sin\alpha \pm \sin\beta)}{\lambda}$$

or: $$\pi \frac{d(\sin\alpha \pm \sin\beta)}{\lambda} = m\pi \qquad m = 0, \pm 1, \pm 2$$

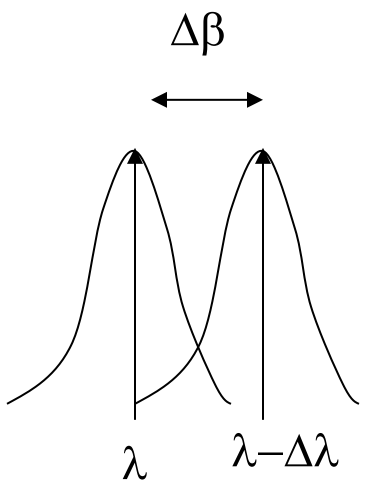
or: $$m\lambda = d(\sin\alpha \pm \sin\beta) \qquad m = 0, \pm 1, \pm 2$$

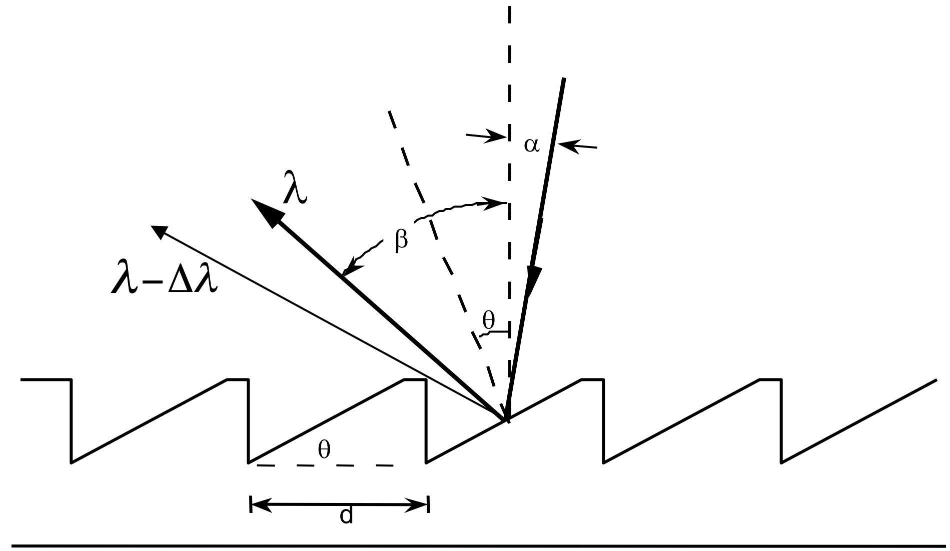
$$\lambda \leq 2d$$

Minimum intensity:

$$(m + \frac{1}{N})\lambda = d(\sin\alpha \pm \sin\beta) \qquad m = 0, \pm 1, \pm 2$$

Relay resolution criteria:





Max: $m\lambda = d(\sin\alpha \pm \sin\beta);$

Min: $(m + \frac{1}{N})(\lambda - \Delta\lambda) = d(\sin\alpha \pm \sin\beta);$

$$m\lambda = m\lambda - m\Delta\lambda + \frac{\lambda}{N} - \frac{\Delta\lambda}{N}$$

$$\frac{\lambda}{\Delta\lambda} = N(m + \frac{1}{N})$$

$$m >> \frac{1}{N},$$

$$\frac{\lambda}{\Delta\lambda} = mN = m\rho l$$

Type	***Capacity***	***Track pitch***	***Wavelength of laser light***
CD	*0.7 GB*	*1.6 μm*	***780 nm (0.780 μm)***
DVD	*4.7 GB*	*0.74 μm*	***650 nm (0.650 μm)***
Blu-ray Disc	*25 GB*	*0.32 μm*	***405 nm (0.405 μm)***

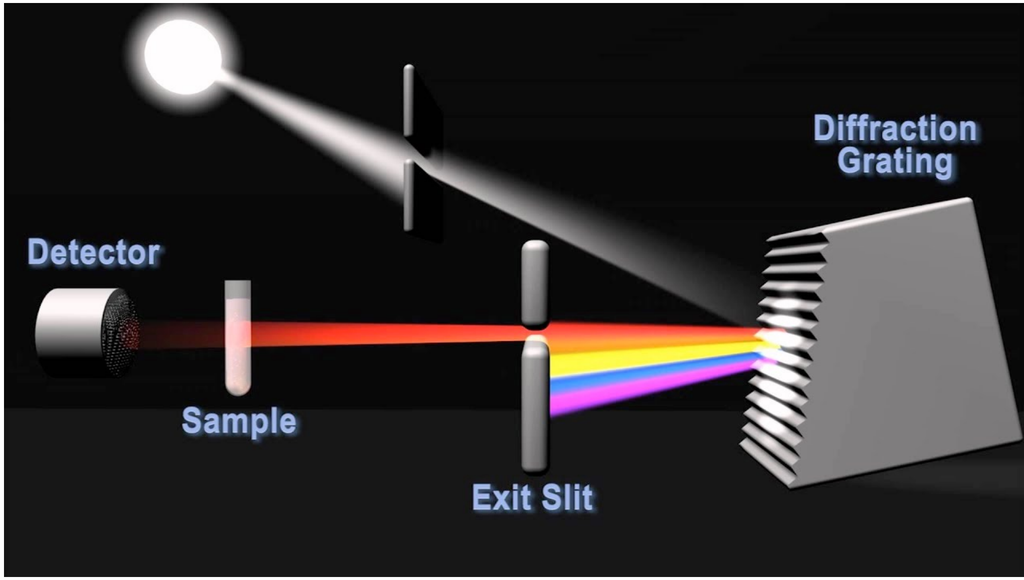
$$m\lambda = d(\sin\alpha \pm \sin\beta) \Rightarrow \lambda = \frac{2d}{m};$$

$$\lambda_1 < 2d,\ \lambda_2 < d\ldots;$$

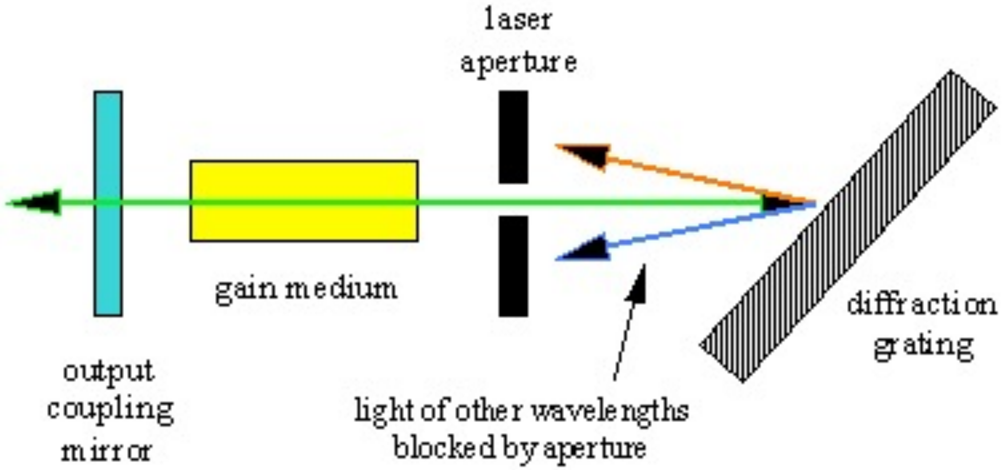
$$m_{\max} \le \frac{2d}{\lambda}.$$

Diffraction grating

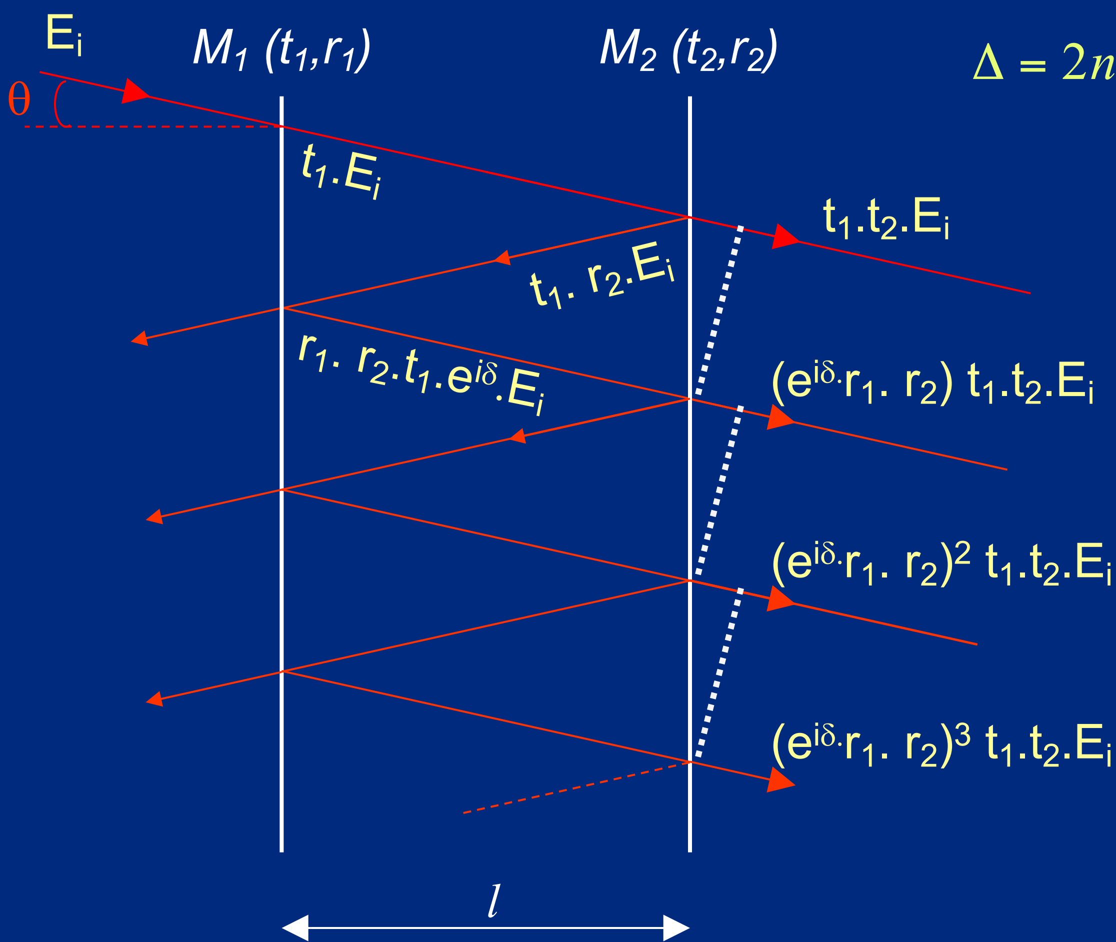
- *Analyze incoming light (spectrometer).*
- *Filter light of one particular wavelength (monochromator).*



- ***Controlling light wavelength in tunable lasers (grating = selective mirror)***



Fabry-Perot interferometer



$$\Delta = 2nl\cos\theta \qquad \delta = \frac{4\pi l}{\lambda}\cos\theta = \frac{4\pi nl}{\lambda_0}\cos\theta$$

$$E_t = E_i t_1 t_2 (1 + r_1 r_2 e^{-i\delta} + (r_1 r_2 e^{i\delta})^2 + \ldots)$$

$$E_t = \frac{E_i t_1 t_2}{1 - r_1 r_2 e^{i\delta}}$$

⇓

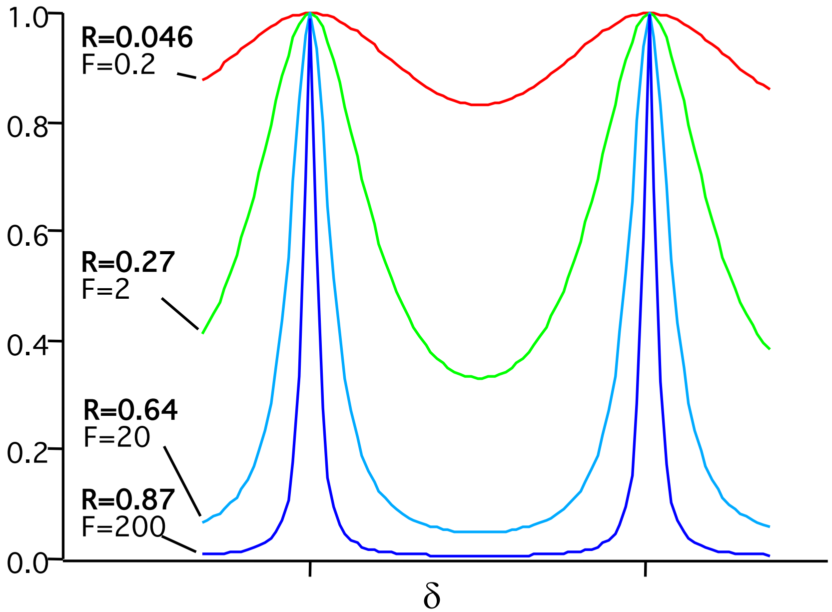
$$I_T = \left|E_T\right|^2 = \frac{I_0 \ \left|t\right|^4}{\left|1 - r^2 \ e^{-i\delta}\right|^2}$$

$$I_T = I_0 \frac{1}{1 - \frac{4R}{(1\text{-}R)^2}\sin^2\frac{\delta}{2}}$$

Airi function

Fabry-Perot interferometer

Airy function



$$I_T = I_0 \frac{1}{1 - \frac{4R}{(1\text{-}R)^2}\sin^2\frac{\delta}{2}} \qquad \delta = \frac{4\pi l}{\lambda}\cos\theta$$

Max: $\delta = 2\,m\,\pi$, $\longrightarrow$ or: $2l\cos\theta = m\lambda$

Max transmittance: $\nu_m = \dfrac{mc}{2l\cos\theta}$, $\tilde{\nu}_m = \dfrac{m}{2l\cos\theta}$

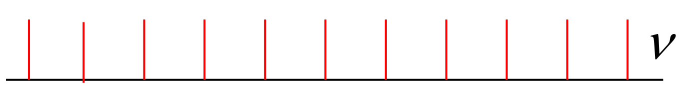
$\nu_m = c/\lambda_m$

$m = 0, 1, 2, \ldots$

Free spectral range: $\Delta\nu = \dfrac{c}{2l}$; $\Delta\tilde{\nu} = \dfrac{1}{2l}$;

FPI is a filter that transmits light with the frequencies multiple to the FSP:

$$\nu_m = m\cdot\frac{c}{2l}\cos\theta$$



Transmission width (and resolution): $\Delta\nu_{1/2} = \dfrac{\Delta\nu}{F} = \dfrac{(1-R)}{2\pi\cdot l\cdot\sqrt{R}}$

Finesse: $F = \dfrac{\pi\sqrt{R}}{(1\text{-}R)}$

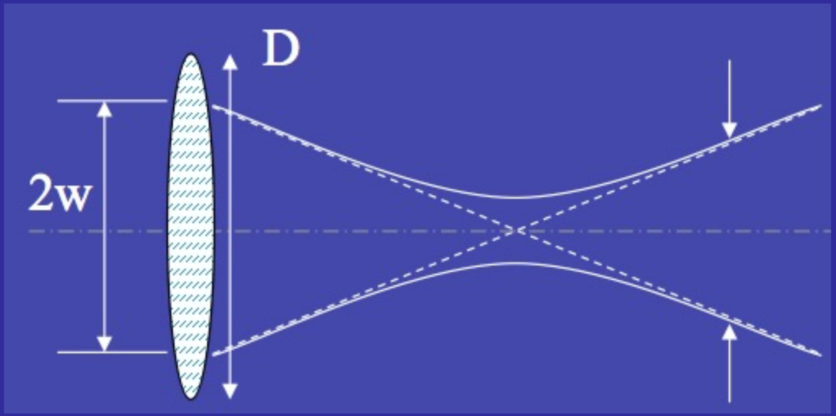
Summary for this lecture

Beam divergence:

$$\theta_B = 2.44\frac{\lambda}{D}$$

The smallest focal point:

$$2w_0 = 2.44\frac{\lambda \cdot F}{D}$$



Intensity for N interfering rays of light:

$$I = I_0^2\frac{\sin^2(N\varphi/2)}{\sin^2(\varphi/2)} \qquad d\sin\alpha_n^{\max} = n\lambda$$

Spectral resolution of grating:

$$\frac{\lambda}{Nd} = \frac{n\Delta\lambda}{d} \Rightarrow \frac{\lambda}{\Delta\lambda} = Nn$$

Transmittance of IFP:

$$\nu_m = m\cdot\frac{c}{2l}\cos\theta$$