Optical methods in chemistry
or
Photon tools for chemical sciences

Session 2:

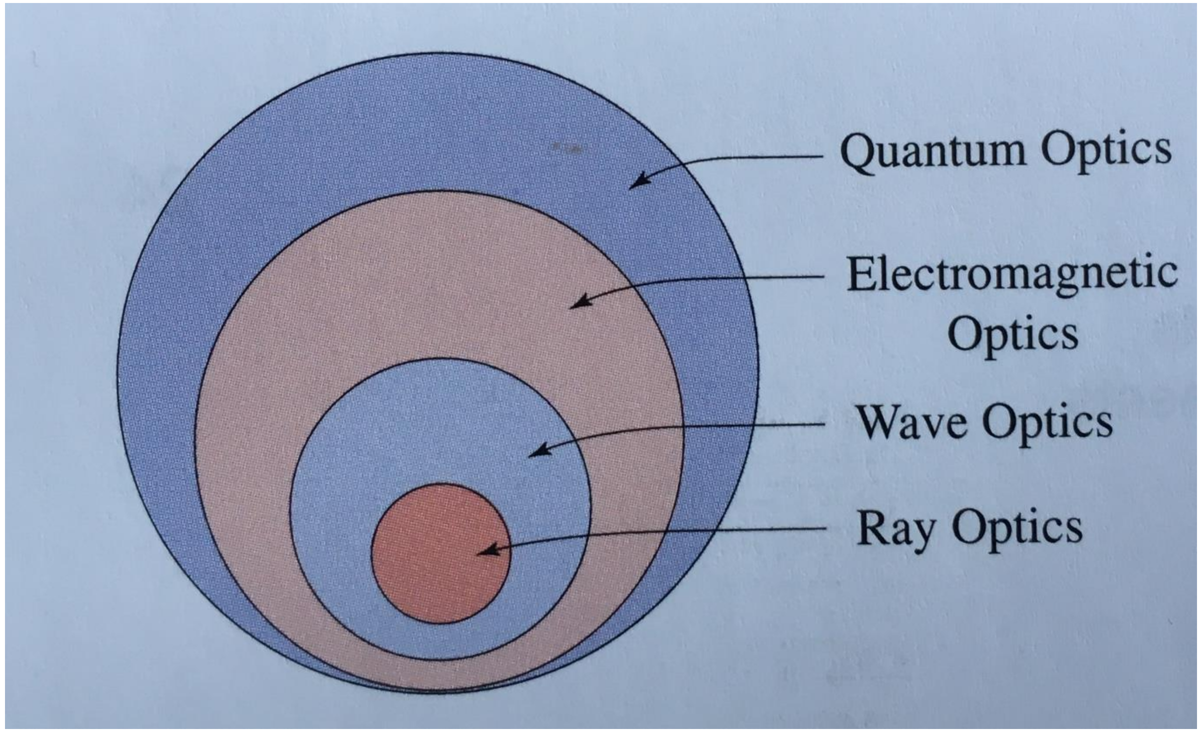
Course layout – contents overview and general structure

- Introduction and ray optics
- Wave optics
- Beams
- From cavities to lasers
- More lasers and optical tweezers
- From diffraction and Fourier optics
- Microscopy
- Spectroscopy
- Electromagnetic optics
- Absorption, dispersion, and non-linear optics
- Ultrafast lasers
- Introduction to x-rays
- X-ray diffraction and spectroscopy
- Summary

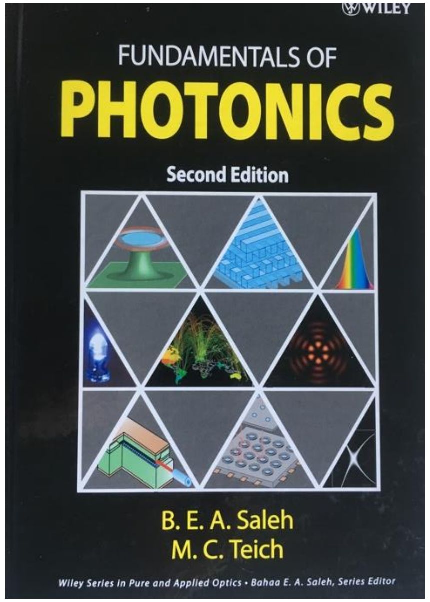
Todays learning goal:

Repeat fundamentals of wave optics

Much exciting science – but you need to know some basics



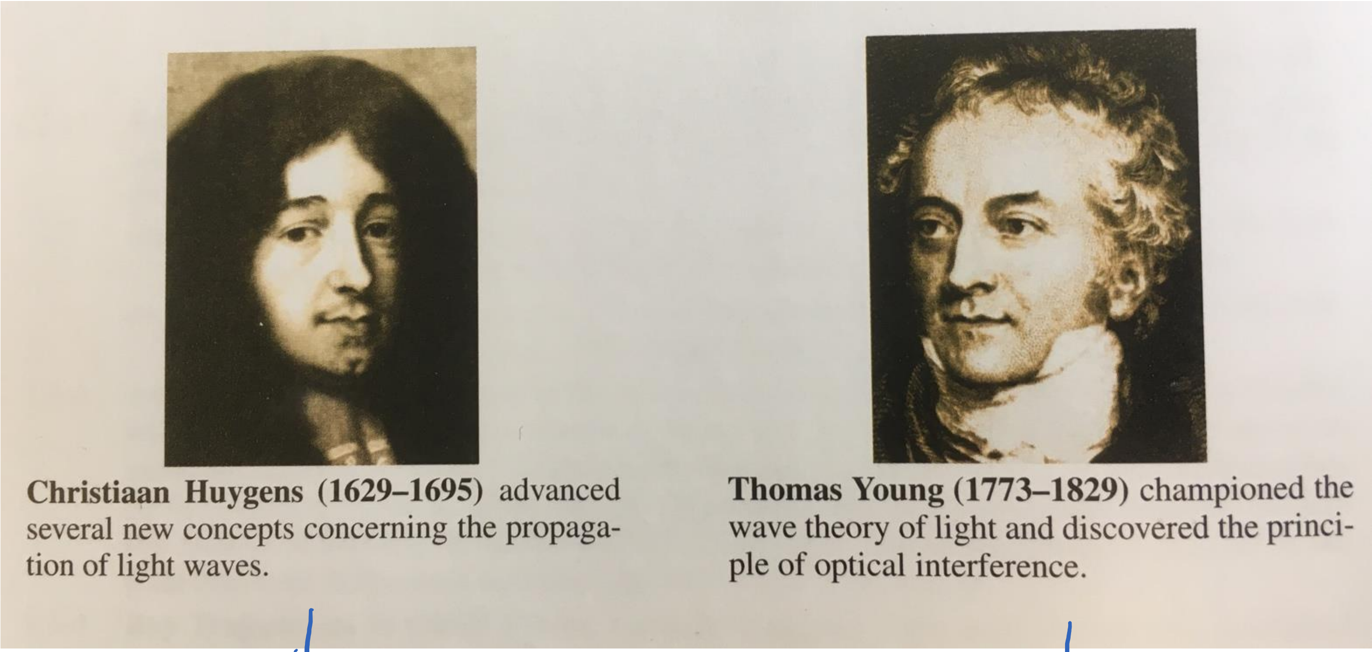
Main source for next topics



Wave optics

Driving question: what is light?!

Last week: Ray optics which is limit of wave optics for infinitesimally short wavelength.



Christiaan Huygens (1629–1695) advanced several new concepts concerning the propagation of light waves.

Thomas Young (1773–1829) championed the wave theory of light and discovered the principle of optical interference.

↓ principles of elementary waves

↓ double slit experiment → wave nature of light

Postulate of wave optics → analogue to last week

- Light propagates in the form of waves, in vacuum light travels with c_o.
- An homogenous transparent medium is characterized by a single constant, the refractive index $n>=1$. In the medium light travels with reduced speed $c = c_0/n$.
- An optical wave is described by a $\boxed{\text{wave}}$ function $\boxed{u(r,t)}$ at position r and time t.

Wave function

The wave function satisfies the (partial) differential equation

$$\nabla^2 u(\vec{r},t) - \frac{1}{c^2}\frac{\partial^2 u(\vec{r},t)}{\partial t^2} = 0$$

Second order differential equation in space & time

∇^2 ____________ Laplace operator in cartesian coordinates

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The principle of superposition applies, i.e., if u1 and u2 are optical waves then

$$u(\vec{r},t) = u_1(\vec{r},t) + u_2(\vec{r},t)$$

Also represents an optical wave

Any function that satisfies this equation ∇ is a possible optical wave !

Optical frequencies and wavelengths

$\Longrightarrow$ relationship to energy

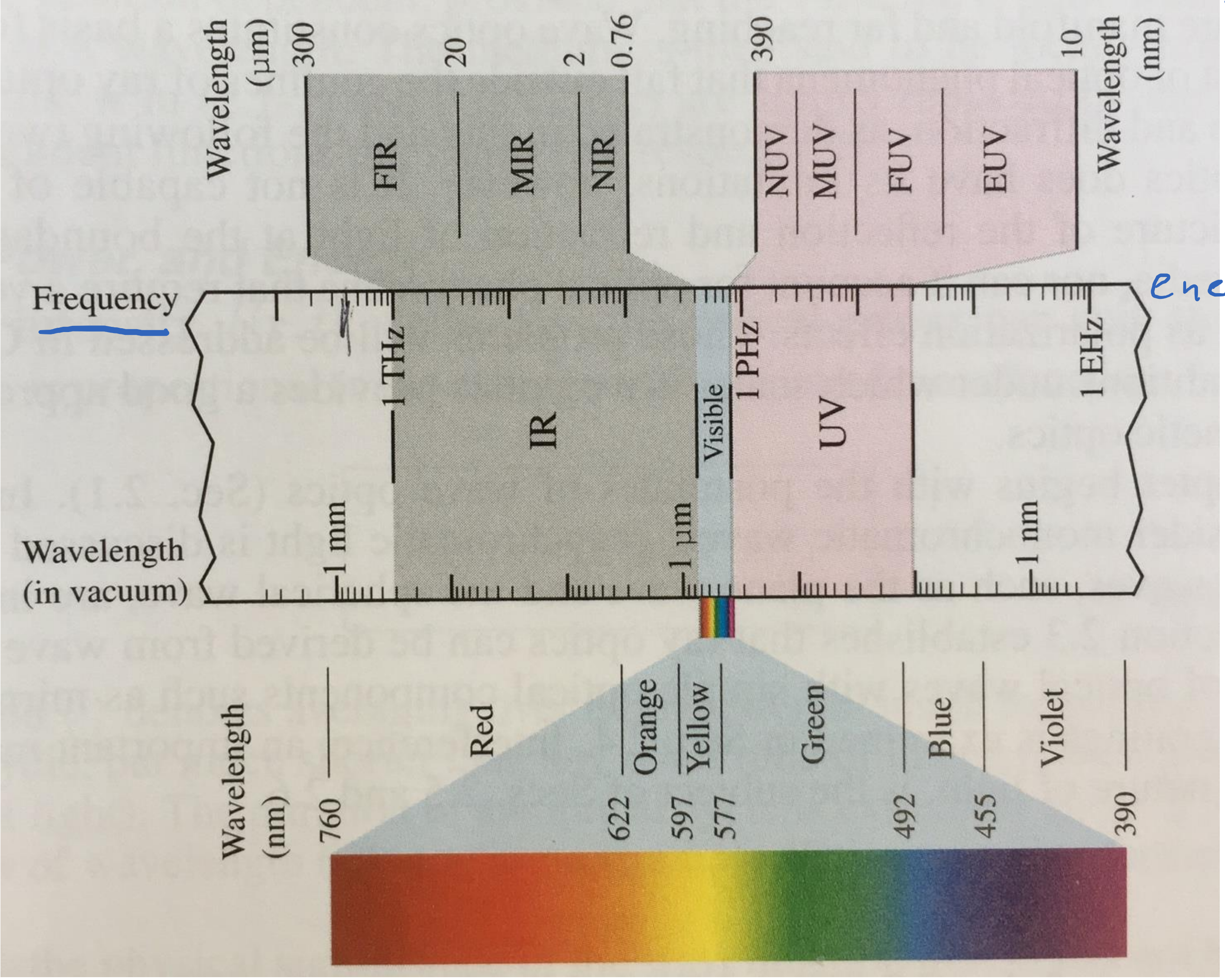
rotational

vibrational

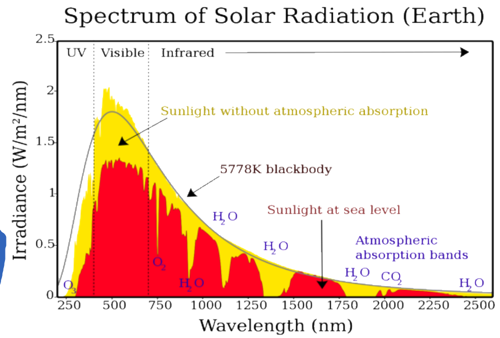
valence excitations

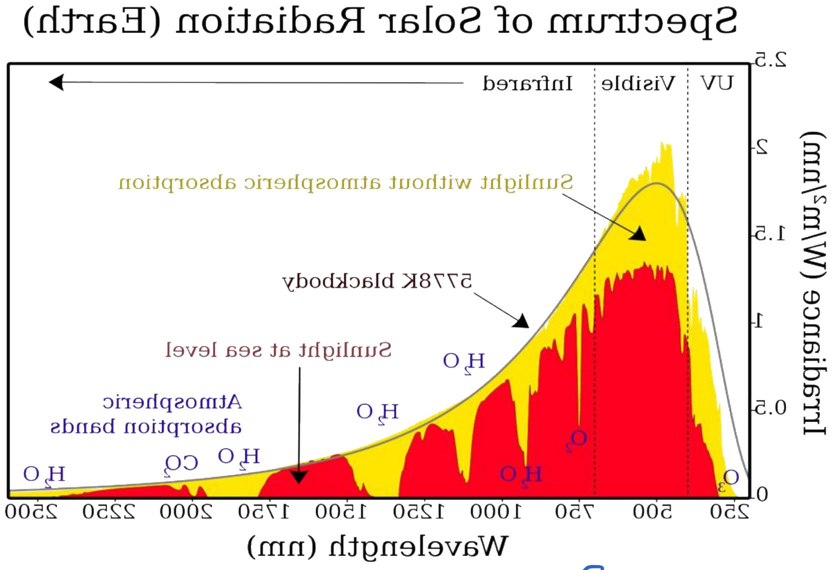
innershell electrons [keV]

$\boxed{1240\,\text{nm} \mathrel{\hat{=}} 1\,\text{eV}}$



energy →





Energy →

Source: wikipedia

Optical intensity, power, energy → Some (important) definitions

- The optical intensity I(r,t) is the optical power per unit area.
  - The unit is $\boxed{\text{Watts/cm}^2}$
  - average of the squared wave function.

$$I(\vec{r},t) = 2\langle u^2(\vec{r},t)\rangle$$

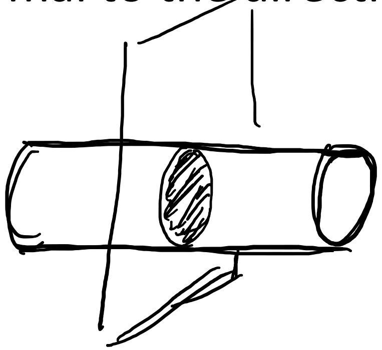
We typically observe intensity average!

Note: for light $\tau_{optical} \sim 2\cdot 10^{-15}\,\text{sec}$ ~ 2 femto sec

faster than any detector (eye)

- The optical power (in units of $\boxed{\text{Watts}}$) flowing into an area A normal to the direction of propagation is the integrated intensity

$$P(t) = \int_A I(\vec{r},t)\, dA$$



- The optical energy (in units of $\boxed{\text{Joules}}$) in a given time interval is the integral of the optical power over the time interval

$$E = \int_t P(t)\, dt$$

Simple example: Monochromatic wave

- For a monochromatic wave the, the wave function reduces to

$$\underset{\text{}}{u(\vec{r},t)} = \underset{\uparrow \atop \text{amplitude}}{a(\vec{r})} \cos(2\pi \underset{\uparrow \atop \text{frequency}}{\nu} t + \underset{\uparrow \atop \text{phase}}{\varphi(\vec{r})})$$

With:

$\omega = 2\pi\nu \rightarrow$ angular frequency $\quad T = \frac{1}{\nu} = \frac{2\pi}{\omega} \rightarrow$ period

amplitude & phase position dependent

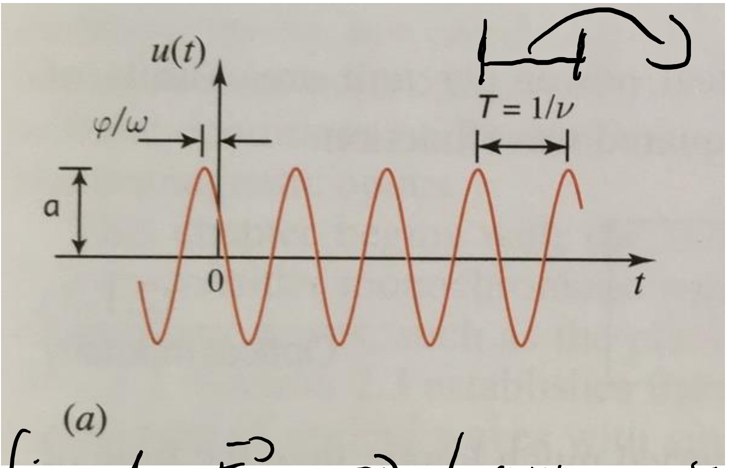
u – harmonic fct in time

- The amplitude and phase are generally position dependent

- Representation of a monochromatic wave <u>at fixed $\vec{r}$!</u>

Period

amplitude



(a)

at fixed $\vec{r} \rightarrow$ harmonic fct in time

Simple example: Monochromativ wave but as complex wave function

- A monochromatic wave can be explained by complex wave function

$$U(\vec{r},t) = \underbrace{U(\vec{r})}_{\text{complex amplitude } U(\vec{r}) = a(\vec{r}) \exp[i\varphi(\vec{r})]} \exp[i2\pi\nu t]$$

↓ more general

Remember

Euler: $e^{ix} = \cos x + i \sin x$

$i = \sqrt{-1}$

- This general description satisfies the

Helmholtz equation: $\nabla^2 U + k^2 \frac{\partial^2}{\partial t^2} U = 0$

With wavenumber k = $\frac{2\pi\nu}{c} = \frac{\omega}{c}$ → Spatial frequency ~ cycles per unit distance

vs

temporal frequency ~ cycles per unit time

- Note intensity: $I(\vec{r}) = |U(\vec{r})|^2$
  - Monochromatic wave intensity is (complex amplitude)^2
  - Intensity does not vary in time

- Note: Wavefronts are surfaces of equal phase

Simple example: Monochromatic wave

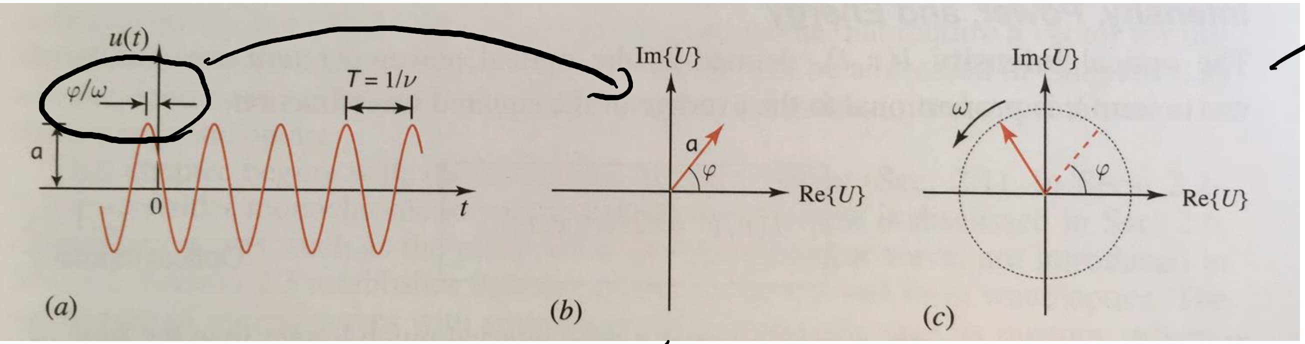
- For a monochromatic wave the, the wave function reduces to

$$U(\vec{r},t) = U(\vec{r}) \exp[i 2\pi \nu t]$$

With: $$U(\vec{r}) = a(\vec{r}) \exp[i \varphi(\vec{r})]$$

- The amplitude and phase are generally position dependent

- Representation of a monochromatic wave → at fixed $\vec{r}$



→ One round in τ

$$\omega = \frac{2\pi}{\tau} = 2\pi\nu$$

$[\text{rad}/\text{sec}]$

→ called "Phasor" | Complex amplitude | Complex wave function

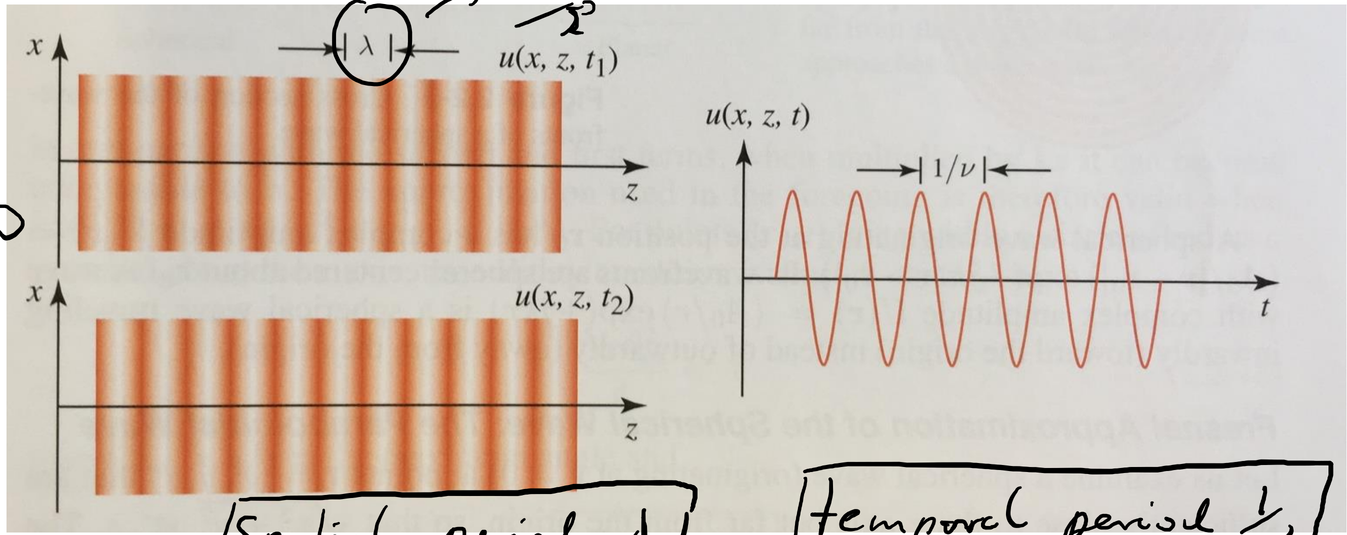
Special case: plane wave → one possible solution for Helmholtz equation

$\lambda = \frac{2\pi}{k}$ ← spatial frequency

k = wave number

$T = \frac{2\pi}{\omega} = \frac{1}{\nu}$ ← temporal frequency

$\frac{2\pi}{\lambda}$



$\boxed{\text{Spatial period } \lambda}$ $\boxed{\text{temporal period } 1/\nu}$

traveling planes in z-direction

Complex amplitude: $U(\vec{r}) = A \exp[-i\vec{k}\vec{r}]$

$= A \exp[-i(k_x x + k_y y + k_z z)]$

$\vec{k}$ = wave vector

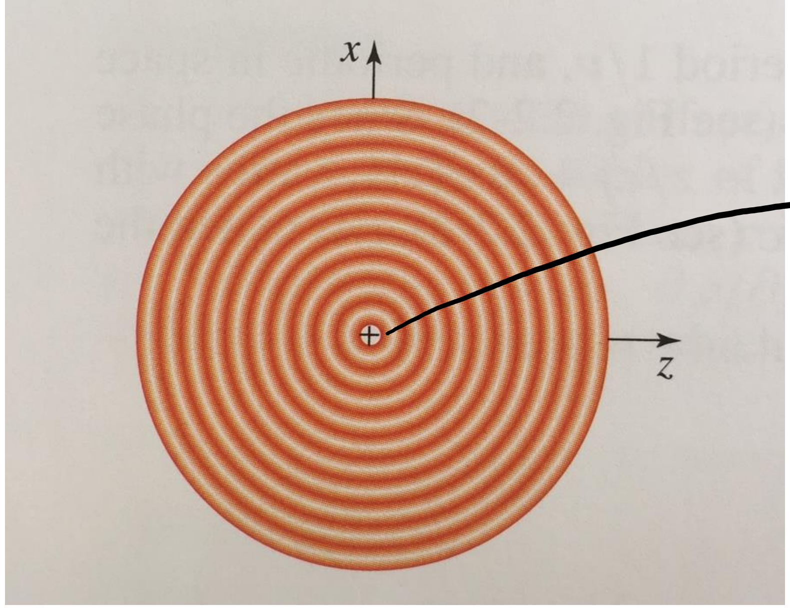
→ wave front are advancing with phase velocity $c = c_0/n$

Plane waves: wavefronts are parallel planes perpendicular to k and separated by λ

For graphical animations visit https://en.wikipedia.org/wiki/Sinusoidal_plane_wave

Special case: spherical wave

→ another solution for Helmholtz equation



→ "point source"

$$U(\vec{r}) = \frac{A_0}{r} \exp[-i\vec{k}\vec{r}]$$

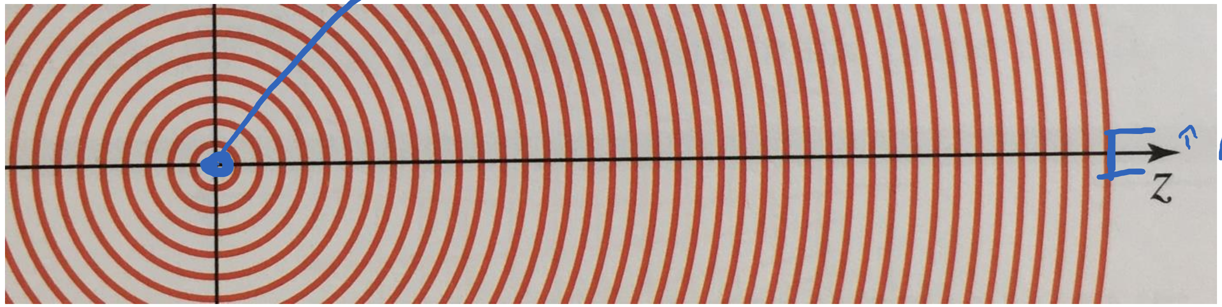
$$I = \frac{|A_0|^2}{r^2} \rightarrow \sim \text{inverse square of distance}$$

Spherical waves: wavefronts are concentric spheres separated by $\lambda=2\pi/k$

For graphical animations visit https://en.wikipedia.org/wiki/Wave_equation#Spherical_waves

Special case: Fresnel approximation

light source → spherical wave



↑ $\sqrt{x^2+y^2} \ll z$

how does wave look in distance?

- Spherical wave close to z-axis but far away from origin

→ "paraxial" waves

→ far from origin $z \gg \sqrt{x^2+y^2}$

→ we can use $r = \sqrt{x^2+y^2+z^2}$ $\quad r = 0$ at origin

→ discuss $e^{-i\vec{k}\vec{r}} \rightsquigarrow e^{-ik\sqrt{(x^2+y^2+z^2)}}$

with "Taylor": $\sqrt{x^2+y^2+z^2}$ & $z \gg x^2+y^2$ ⇒ new variable $\theta^2 = \frac{x^2+y^2}{z^2} \ll 1$

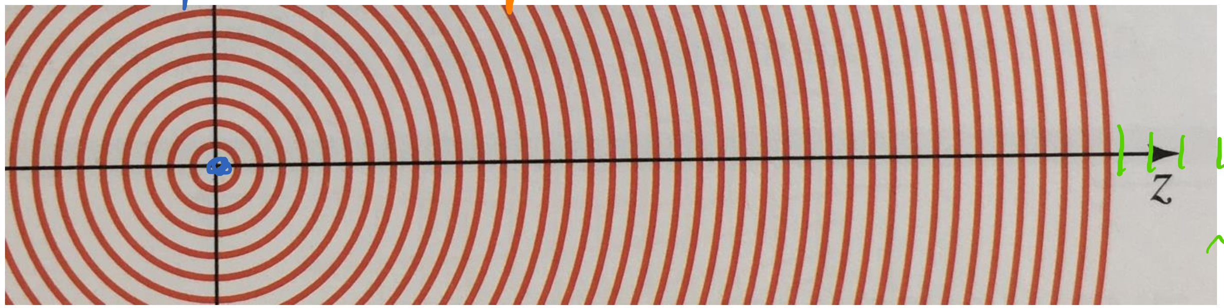
$\sqrt{1+\theta^2} \rightsquigarrow \left(1+\frac{\theta^2}{2}-\frac{\theta^4}{4}\dots\right)$

↳ $z\sqrt{\frac{x^2+y^2}{z^2}+1} = z\sqrt{1+\theta^2} \approx z + \frac{x^2+y^2}{2z} \sim \sqrt{x^2+y^2+z^2}$

Special case: Fresnel approximation

$z \gg x^2+y^2$
and far from origin
and close to axis (paraxial)

spherical parabolic



~ plane wave

- Spherical wave close to z-axis but far away from origin

Now back to spherical wave and with $r \approx z + \frac{x^2+y^2}{2z}$

$$U(r) = \frac{A_0}{r} \exp\left[-i\vec{k}\vec{r}\right]$$

$$= \frac{A_0}{z} \exp\left[-ikz\right] \exp\left[-ik\frac{x^2+y^2}{2z}\right]$$

Amplitude varies slowly with z

Looks like a plane wave

parabolic wave with $z \gg 0 \to 0$

Comment: Taylor series

Reminder of math concept

Representation of a fct as a sum of its derivatives

at a single point(!)

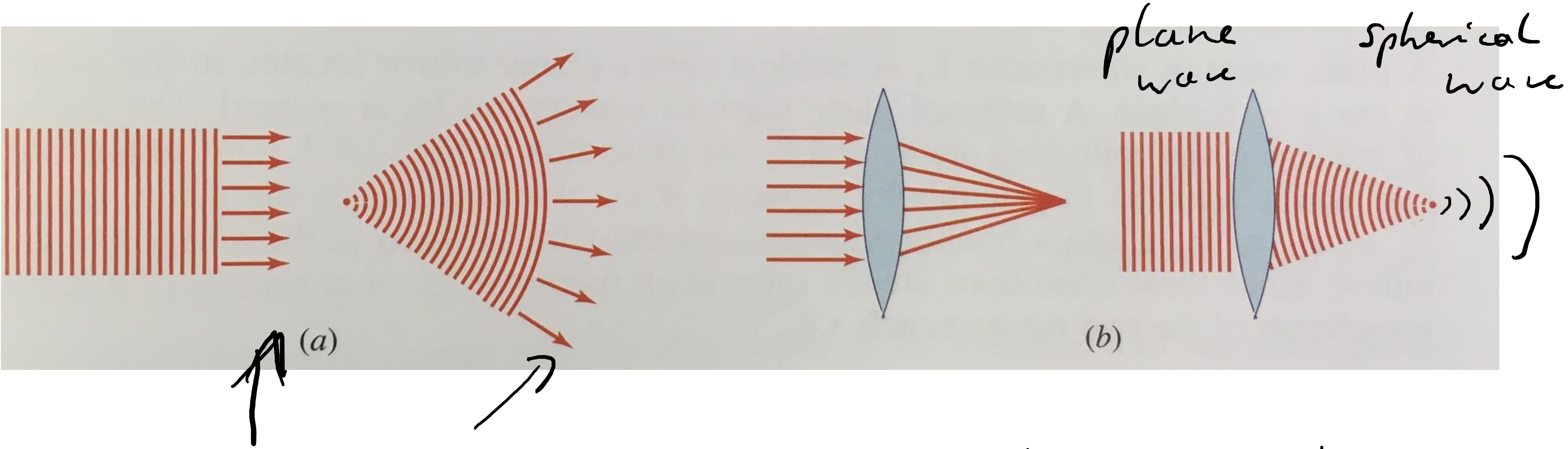
$$f(a) + \frac{f'(a)}{1!}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \ldots$$

$$\sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!}(x-a)^n$$

Examples $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots$

$$\underset{x \ll 1}{\sqrt{1+x}} = 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \ldots$$

From ray to wave optics → ray optics are the limits of wave optics

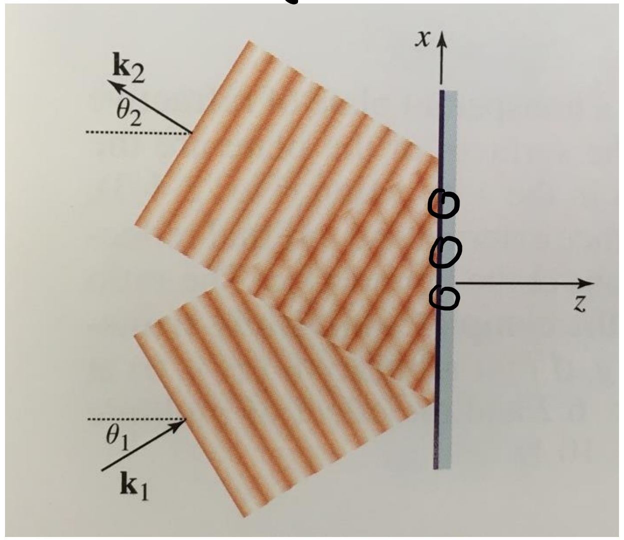


rays of ray optics → orthogonal to wavefronts

What happens after focal point?

Wave optics and simple optical components

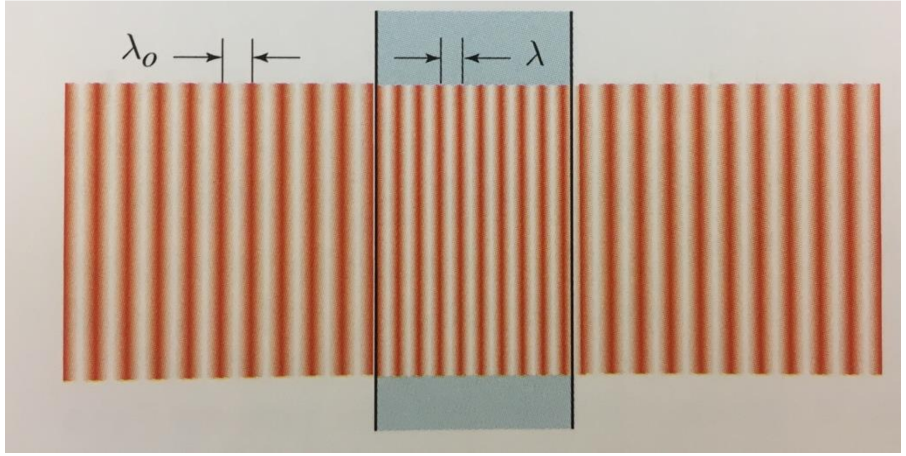
reflection



phase matching

↓

angles of incident and reflection are equal



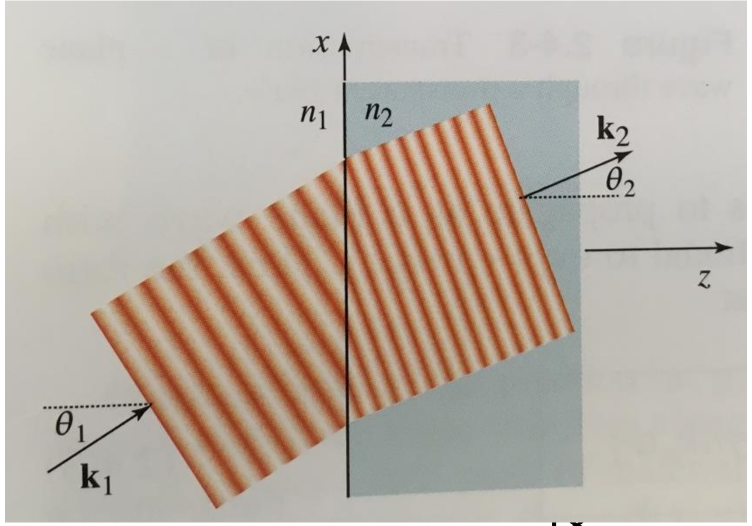
Change of optical density

$$\lambda = \frac{\lambda_o}{n}$$

wave fronts match at boundary

↓

Snell's Law



Interference of two waves

When two monochromatic waves with complex amplitudes U_1 and U_2 are superimposed, the result ia a monochromatic wave of the same frequency that has a complex amplitude

$$U(r) = U_1(r) + U_2(r)$$

The intensity of the resulting wave is:

$$I = |U|^2 = |U_1 + U_2|^2 \leftarrow \text{depends on phase!}$$

Resulting in the interference equation:

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\varphi$$

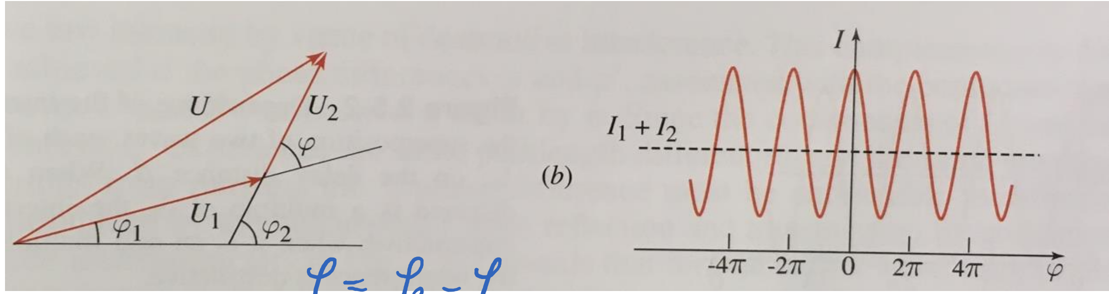
interference term

similar intensities, special cases

$$I + I + 2\sqrt{I^2} \cdot 1 \quad \Big| \quad \cos 0 \to 1$$

$$\cdot\, 0 \quad \Big| \quad \cos \tfrac{\pi}{2} \to 0$$

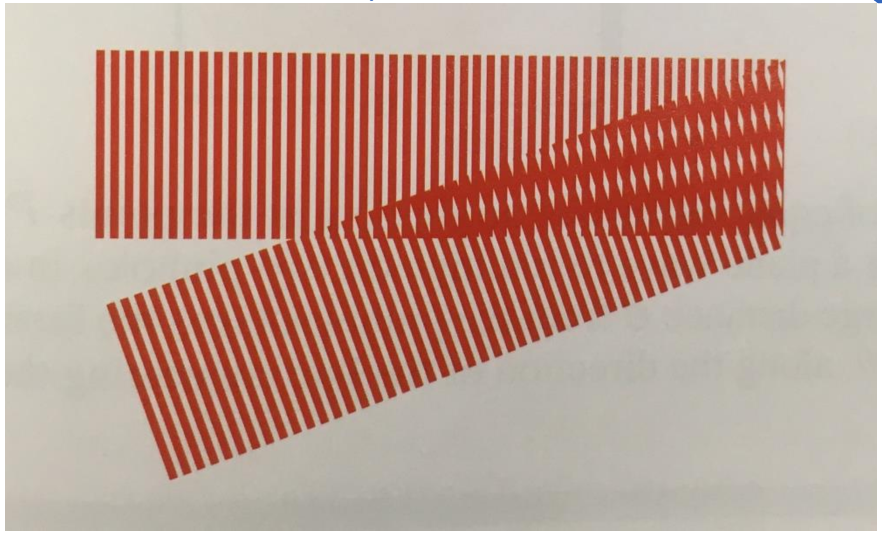
$$\cdot\, (-1) \quad \Big| \quad \cos \pi \to -1$$



$\varphi = \varphi_2 - \varphi_1$

Interference: Some examples

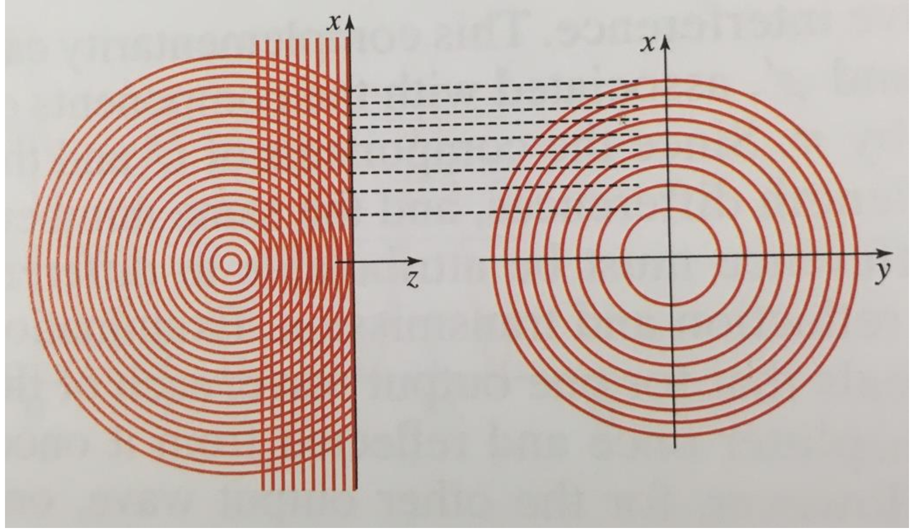
two plane waves @ angle



$\Downarrow$

transient grating
in pulsed laser exps

plane wave + spherical wave



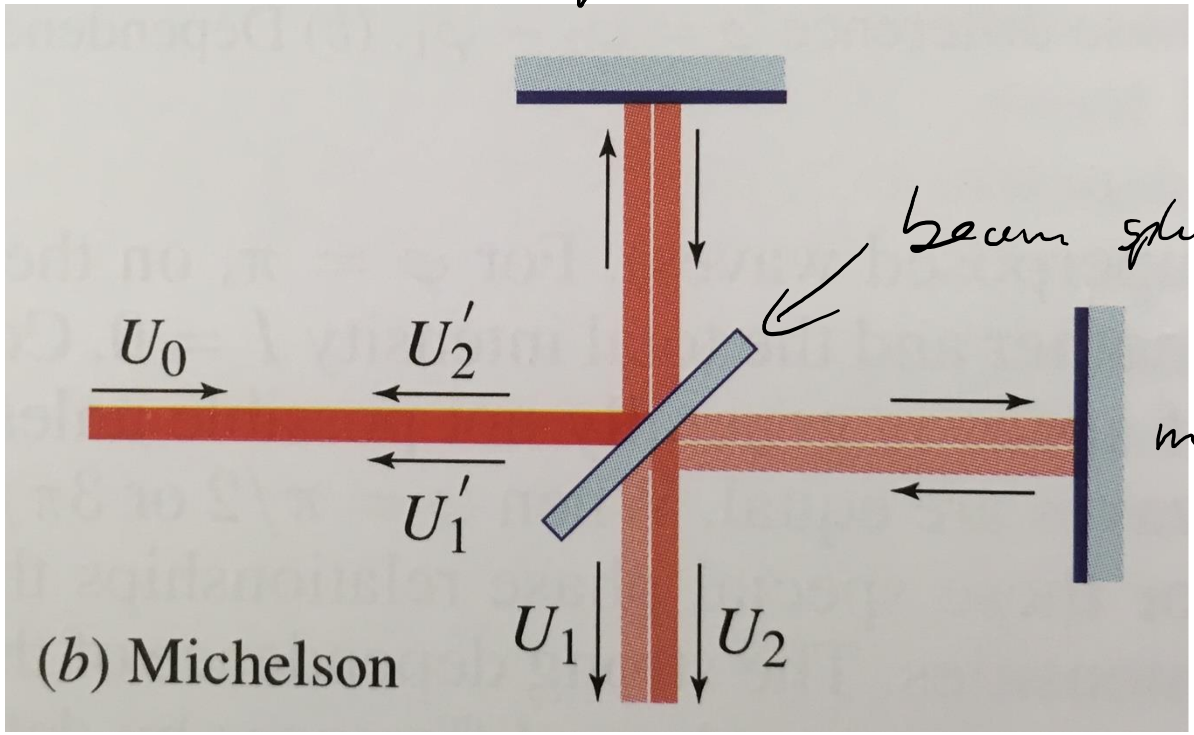
$\Uparrow$

interference
pattern

Interferometer, example Michelson

(Neglecting phase shift at beam splitter for now)

mirror



beam splitter

mirror

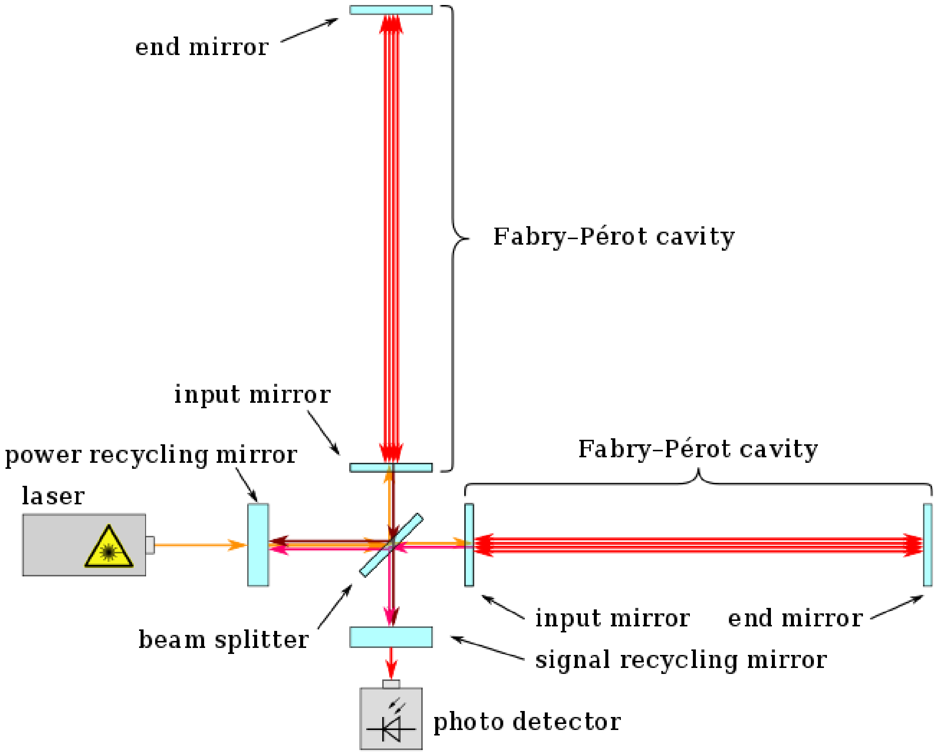
What do you expect for equal length?

$\Delta l = 0$?

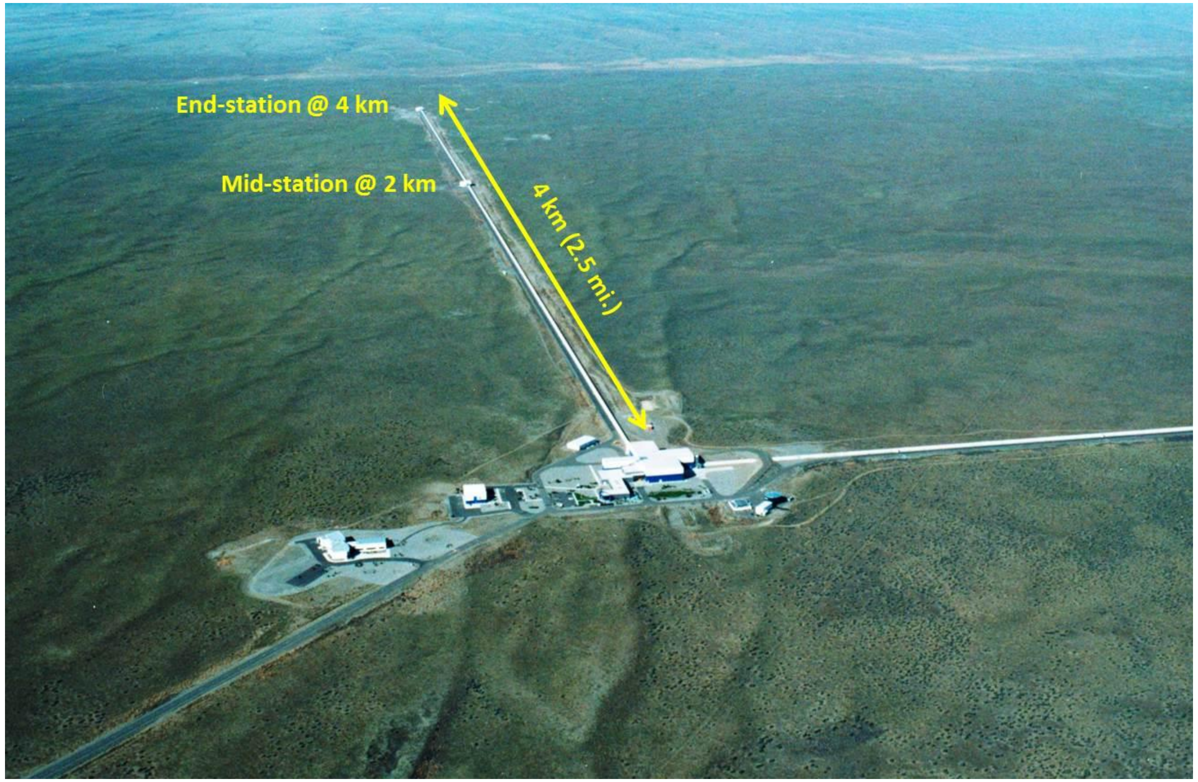
$\Delta l = \frac{\lambda}{2}$?

Nice demonstration: https://www.youtube.com/watch?v=j-u3IEgcTiQ

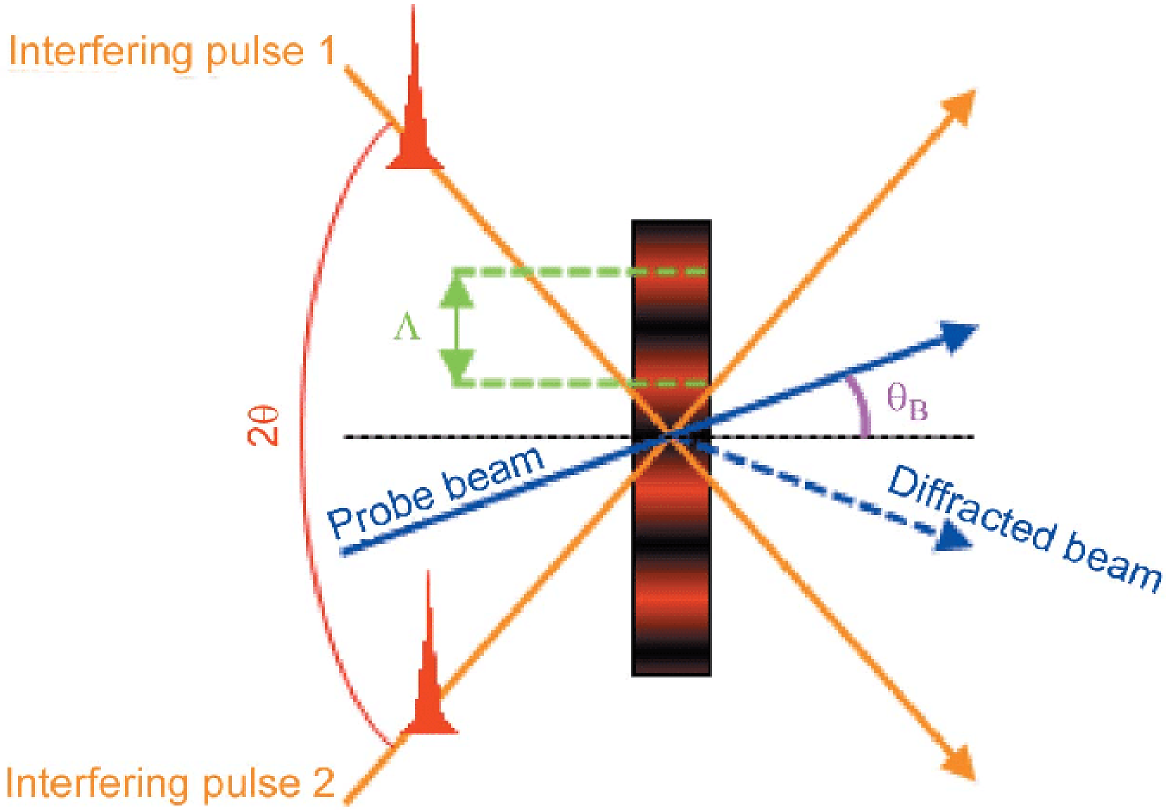
Guess what this is? Or: How precise can interferometers be?



Yes, this is a schematic of LIGO
(Laser Interferometer Gravitational-Wave Observatory)



An ultrafast example: transient grating spectroscopy



c.f.
slide 20

Source: Fermi FEL at Elletra

Optical beating

- Optical wave composed of two monochromatic waves

$$U(t) = \sqrt{I_1} \exp[i 2\pi \nu_1 t] + \sqrt{I_2} \exp[i 2\pi \nu_2 t]$$

$I = |A|^2$

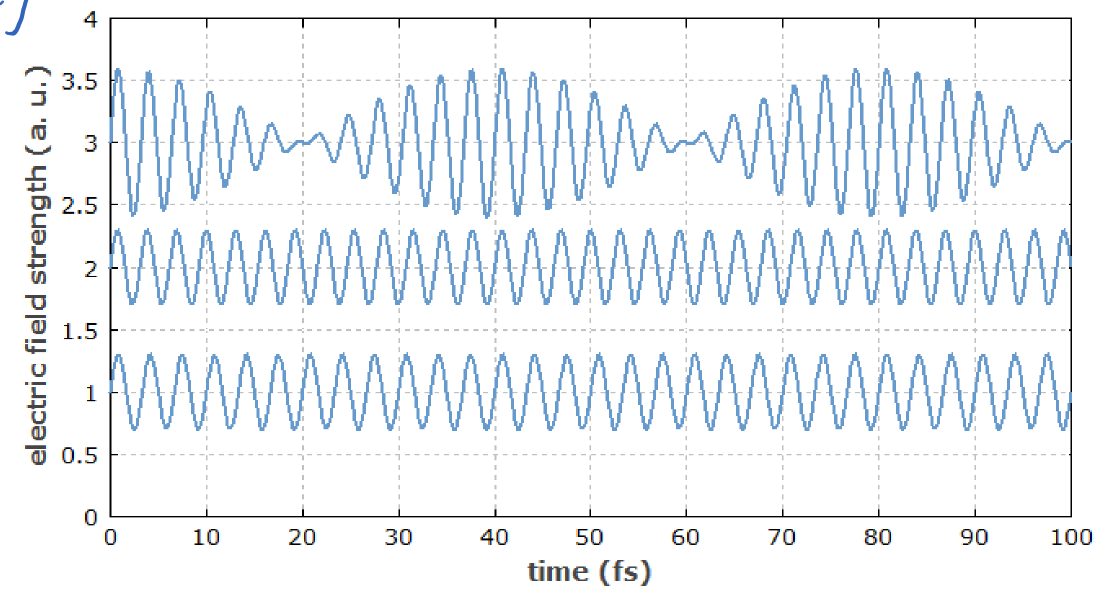
$\rightarrow A = \sqrt{I}$

- Intensity of this wave is

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos(2\pi(\nu_2 - \nu_1) t)$$

- With beat frequency

$$|\nu_2 - \nu_1|$$

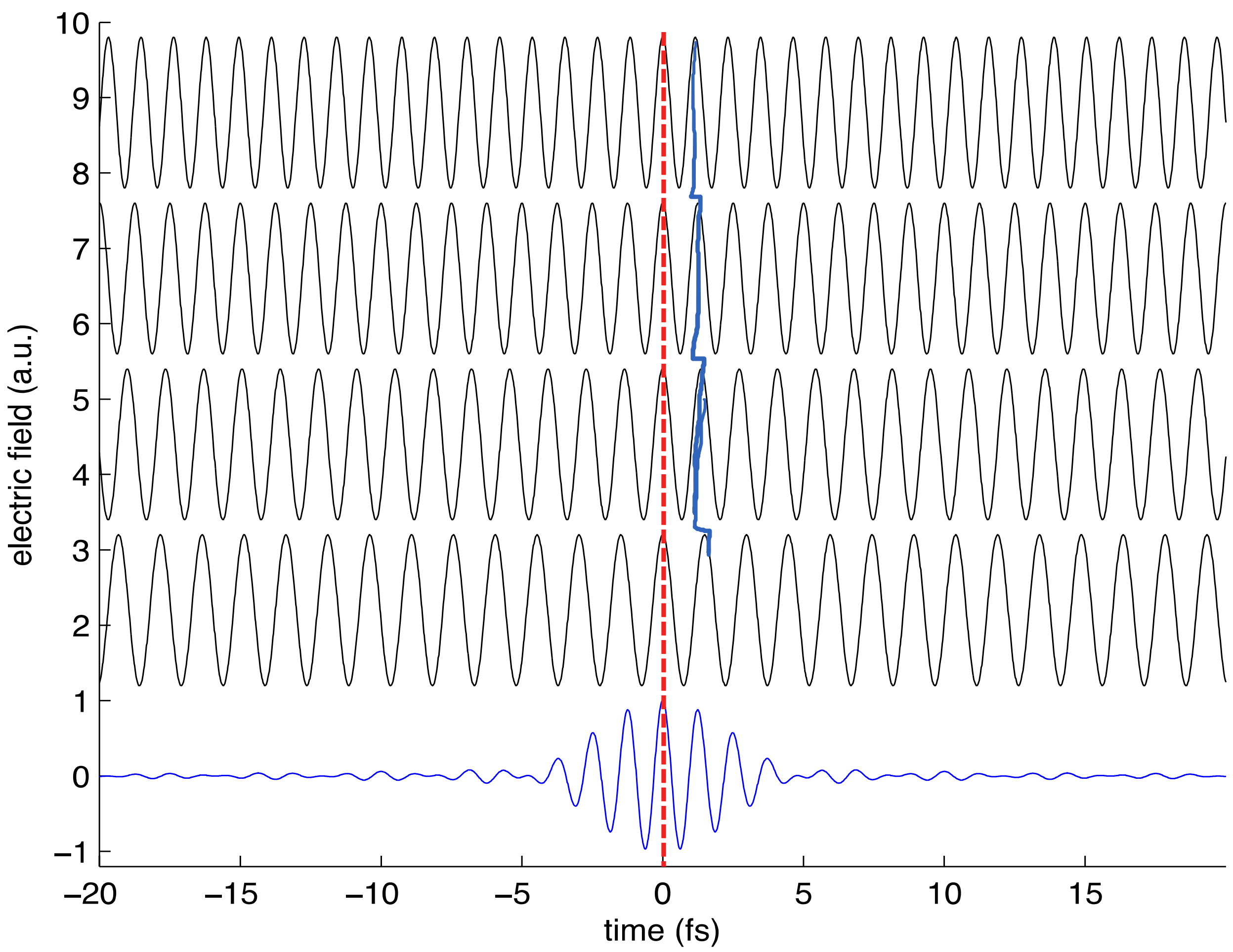


- Note: known as light beating, optical mixing, heterodyning, and others

Detectors are sensitive to intensity!

$\rightarrow$ signals at difference of frequencies

Now do this with many frequencies – short pulse



Coherent superposition of plane waves

↓

short pulse

↓

many frequencies, fixed phase relationship

Note the shorter the pulse, the more frequencies needed

Pulsed light

- Formal description: Add time varying complex envelope A(t) to wave function

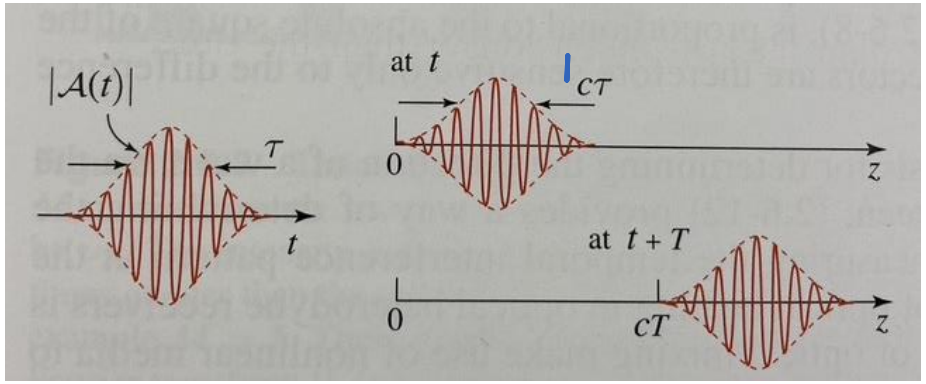
central optical frequency

$$U(\vec{r},t) = A(t-\tfrac{z}{c}) \exp\left[i 2\pi \nu_0 (t-\tfrac{z}{c})\right]$$

complex envelope A(t), time varying fct

wave packet

travelling in time

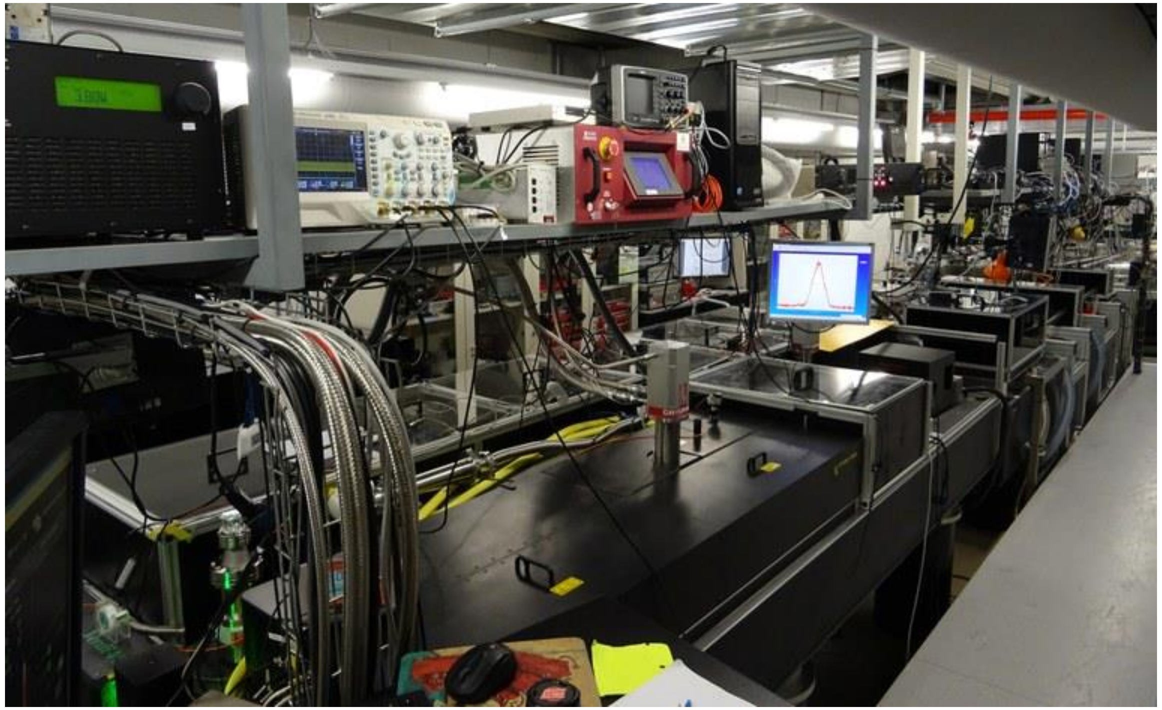


Excursion: High-intensity lasers

Modern commercial laser

$E = 10\,mJ/\text{pulse}$, $100\ Hz$

$P_{average} \rightarrow \frac{10\,mJ \cdot 100}{sec} = 1\,J/sec = 1\,W$



Lacus laser, EPFL

But pulses are short, power in pulse high!

$\tau = 50\,fsec$

$\Rightarrow P = \frac{10^{-2}\,J}{50 \cdot 10^{-15}\,sec} = \frac{1}{5} \cdot 10^{-2+14}\,J/sec = 2 \cdot 10^{11}\,W$

$= 200\ GW$

Now focus to $100\ \mu m^2$

$I = \frac{2 \cdot 10^{11}\,W}{100 \cdot 10^{-4}\,cm^2} = 10^{15}\,W/cm^2 \rightarrow$ Laser field similar to atomic potential

The end.