

Optical methods in chemistry  
or  
Photon tools for chemical sciences

Session 1:  
Introduction and ray optics

# Contact

Christoph Bostedt

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- Office location and hours
  - CH B1 375 (Bâtiment CH)
  - Thursday afternoon 15:00 – 16:00
- Teaching assistant
  - Hankai Zhang (LUXS)
  - hankai.zhang@epfl.ch

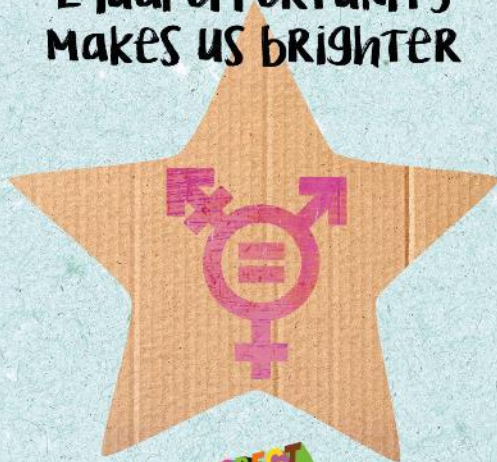


# Formalities

- 2 hours lectures and 1 hours exercise
- Written exam
- 3 Credits
  - 75-90 hours work load
  - 15-20 hours exam prep
  - 4-5 hours weekly investment
- Pass requirements
  - 60% total score
  - Exercise/homework is participation score
  - Final grade 80% final exam and 20% exercise/homework

Some important general remarks

EQUAL OPPORTUNITY  
MAKES US BRIGHTER



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DIVERSITY IS  
OUR STRENGTH



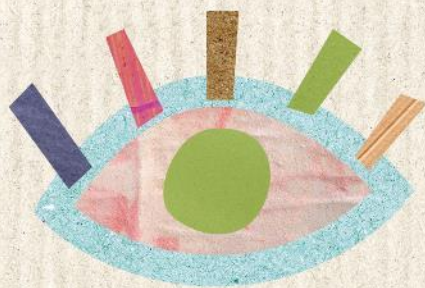
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LISTEN AND DARE  
TO SPEAK UP



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LOOK OUT  
FOR EACH OTHER



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KINDNESS  
BRINGS SERENITY



© EPFL

TOGETHER  
WE GO FURTHER



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Back to chemistry, optics, this course

# Short introduction

- Shared position between EPFL and Paul-Scherrer-Institute (PSI) in Villigen (Aargau)
- Spent 3-4 days at PSI and 1-2 at EPFL
- At PSI, Head of Laboratory for Femtochemistry  
<https://www.psi.ch/en/lfsf>
- At EPFL, Head of Laboratory for Ultrafast X-ray Sciences  
<https://luxs.epfl.ch>
- Prior: Argonne Natl Lab / Northwestern University, SLAC / Stanford University, TU Berlin
- Trained as a physicist but now part of chemistry faculty at EPFL
- In general I use large, accelerator-based light sources for ultrafast spectroscopy and structural analysis



## Break the ice: Student introduction, expectation, wishes.

- I did my bachelor degree at...
- I chose P-CHEM (this course) because...
- I hope to take away the following from the course...
- I plan a career in academia, industry RD, management, education

Some more questions, I am comfortable with...:

$$\nabla^2 u - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} = 0 \quad \text{diff. equation / wave equation}$$

$$f(x) = \int_{-\infty}^{\infty} \tilde{f}(\tilde{x}) e^{-2\pi i \tilde{x}} d\tilde{x} \quad \text{Fourier integral}$$

$$\Delta E \cdot \Delta t \approx \hbar \quad \text{Heisenberg uncertainty principle}$$

$$\sqrt{\frac{\epsilon}{\epsilon_0} \cdot \frac{\mu}{\mu_0}} = \frac{c}{c_0} = n \quad \text{refractive index in EM description}$$

diffraction limit

# 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

I am familiar with the concepts of

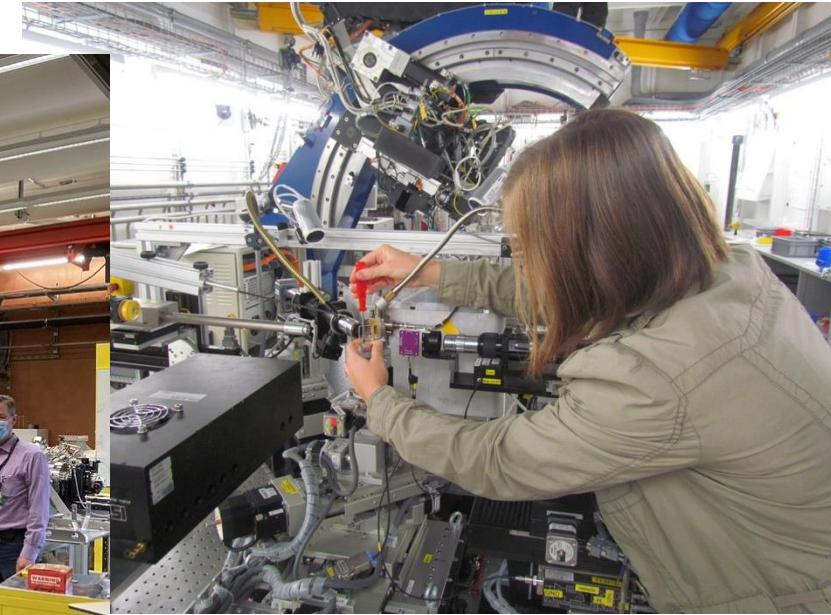
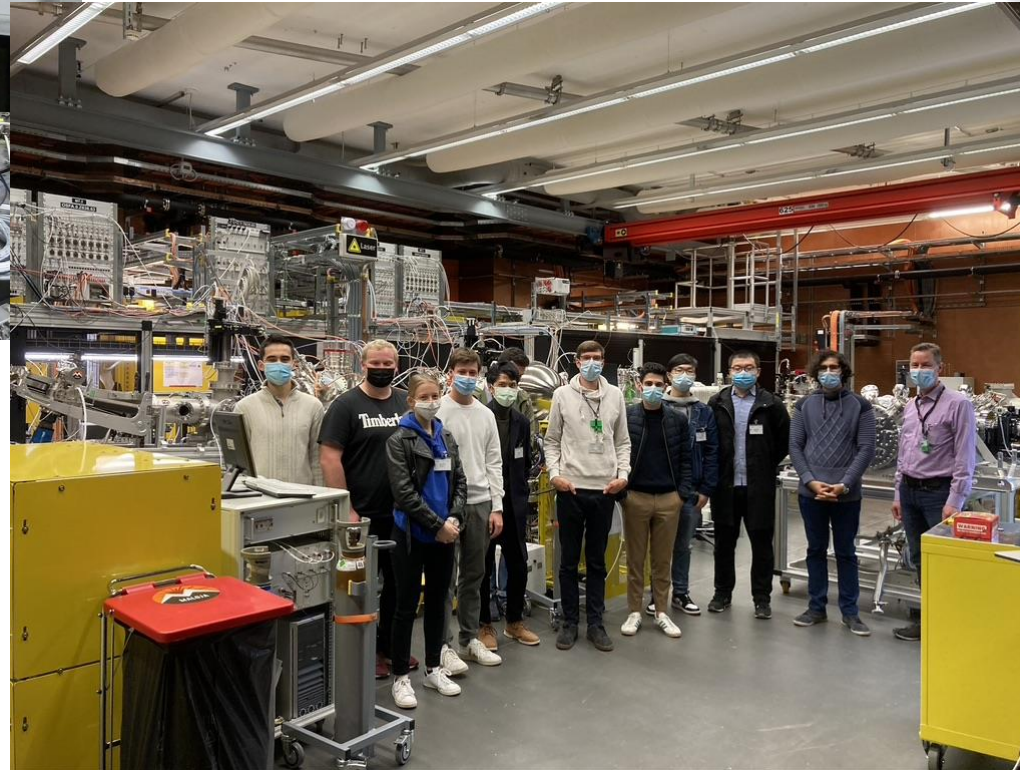
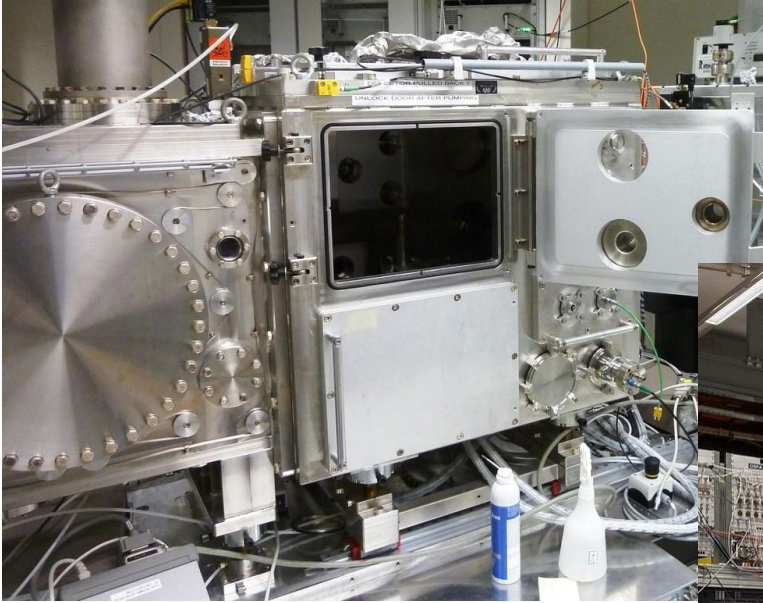
- A. Ray optics, I can draw classical optical systems
- B. Wave optics, diffraction, interference
- C. Beam optics, Rayleigh length, optical modes
- D. Lasers and applications

# Course layout - teaching

- Previous courses
  - Used powerpoint only – information overload
  - Blackboard lectures – very educational but not ideal incorporation of graphics / media
- Here:
  - Prepare powerpoint skeleton
  - Fill in blanks with e-pen during lecture
  - Full pdf available after lecture
- Feedback and suggestions always welcome!
- Literature I mostly rely on (to be updated)
  - Saleh Teich: Photonics
  - Nielsen Mc Morrow: Elements of Modern X-ray Physics
  - Hollas: Modern Spectroscopy
  - Websites etc as indicated in script



Excursion to PSI –  
the multidisciplinary research  
center of the EPF/ETH Domain



# Light, X-rays, Lasers and Chemistry

A bit of a motivation

Absorption and emission of light has always been prime diagnostics for chemistry

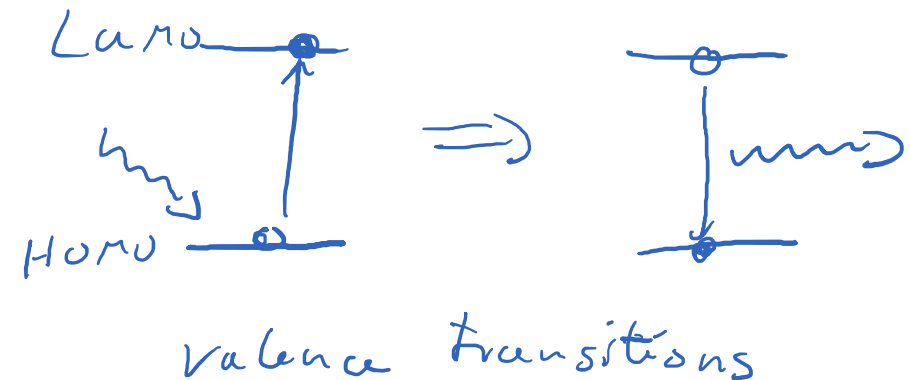


[https://www.youtube.com/watch?v=1EXr\\_L7Ojqg](https://www.youtube.com/watch?v=1EXr_L7Ojqg)

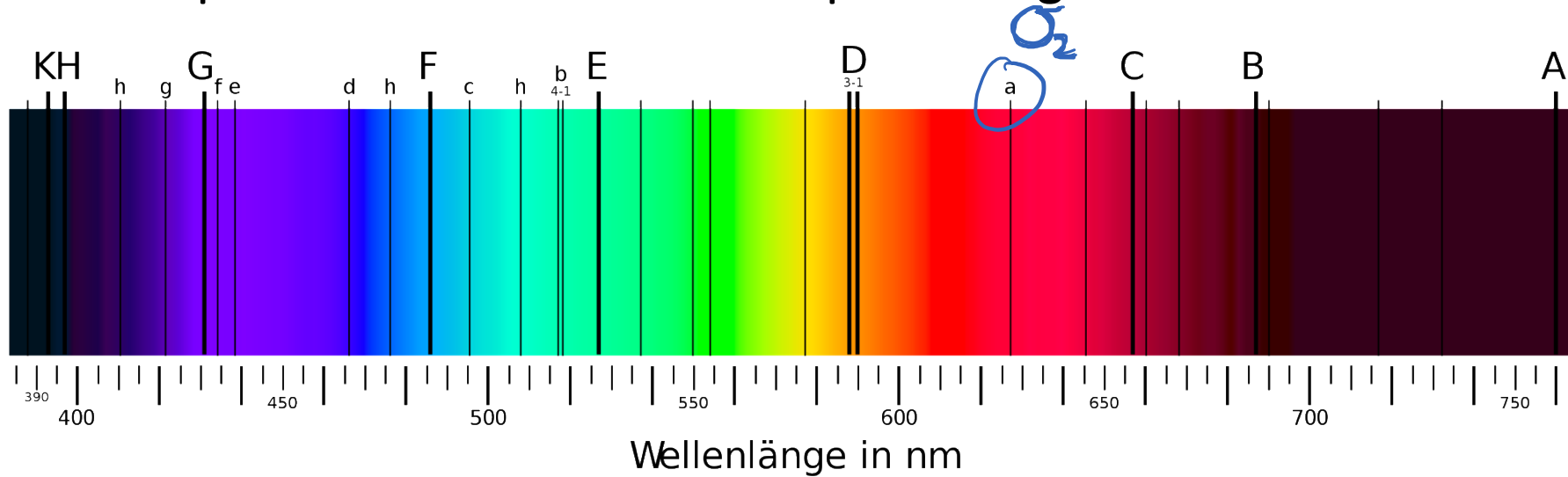
How does it work?

What do the colors tell you?

Is it quantitative or qualitative?



# Inverse process: characteristic absorption of light



Fraunhofer Lines

→ solar spectrum  
↓  
should be continuous  
↓  
absorption lines  
↓  
elements

| Symbol                | Element        | Wellenlänge in nm | Symbol | Element         | Wellenlänge in nm |
|-----------------------|----------------|-------------------|--------|-----------------|-------------------|
| y                     | O <sub>2</sub> | 898,765           | c      | Fe              | 495,761           |
| Z                     | O <sub>2</sub> | 822,696           | F      | H β             | 486,134           |
| A                     | O <sub>2</sub> | 759,370           | d      | Fe              | 466,814           |
| B                     | O <sub>2</sub> | 686,719           | e      | Fe              | 438,355           |
| C                     | H α            | 656,281           | G'     | H γ             | 434,047           |
| a                     | O <sub>2</sub> | 627,661           | G      | Fe              | 430,790           |
| D <sub>1</sub>        | Na             | 589,594           | G      | Ca              | 430,774           |
| D <sub>2</sub>        | Na             | 588,997           | h      | H δ             | 410,175           |
| D <sub>3</sub> oder d | He             | 587,562           | H      | Ca <sup>+</sup> | 396,847           |
| e                     | Hg             | 546,073           | K      | Ca <sup>+</sup> | 393,368           |
| E <sub>2</sub>        | Fe             | 527,039           | L      | Fe              | 382,044           |
| b <sub>1</sub>        | Mg             | 518,362           | N      | Fe              | 358,121           |
| b <sub>2</sub>        | Mg             | 517,270           | P      | Ti <sup>+</sup> | 336,112           |
| b <sub>3</sub>        | Fe             | 516,891           | T      | Fe              | 302,108           |
| b <sub>4</sub>        | Fe             | 516,751           | t      | Ni              | 299,444           |
| b <sub>4</sub>        | Mg             | 516,733           |        |                 |                   |

Absorption lines in solar spectrum for elemental analysis

Mix of solar and terrestrial elements

Can you do this with any light source, e.g. your LED flashlamp?

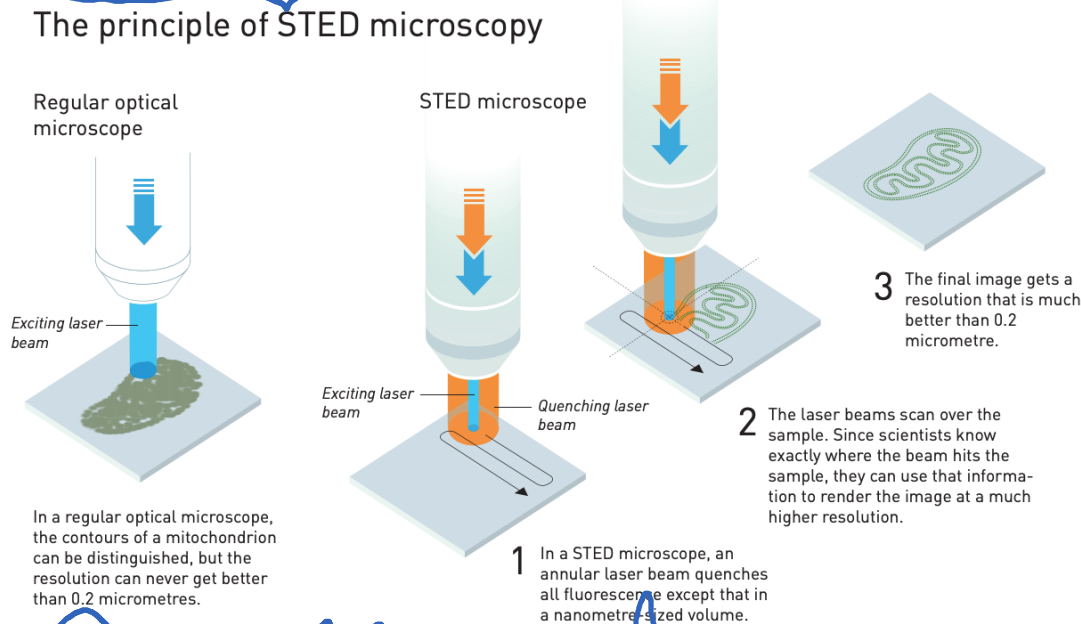
What is special about the solar spectrum?

↓  
continuous

# Recent examples of applications of light to chemistry

*stimulated emission depletion spectroscopy*

The principle of STED microscopy



**Eric Betzig, Stefan W. Hell and William E. Moerner** are awarded the Nobel Prize in Chemistry 2014 for having **bypassed a presumed scientific limitation stipulating that an optical microscope can never yield a resolution better than 0.2 micrometres.** Using the fluorescence of molecules, scientists can now monitor the interplay between individual molecules inside cells; they can observe disease-related proteins aggregate and they can track cell division at the nanolevel.



© Nobel Media AB. Photo: A. Mahmoud  
**Eric Betzig**  
Prize share: 1/3



© Nobel Media AB. Photo: A. Mahmoud  
**Stefan W. Hell**  
Prize share: 1/3



© Nobel Media AB. Photo: A. Mahmoud  
**William E. Moerner**  
Prize share: 1/3

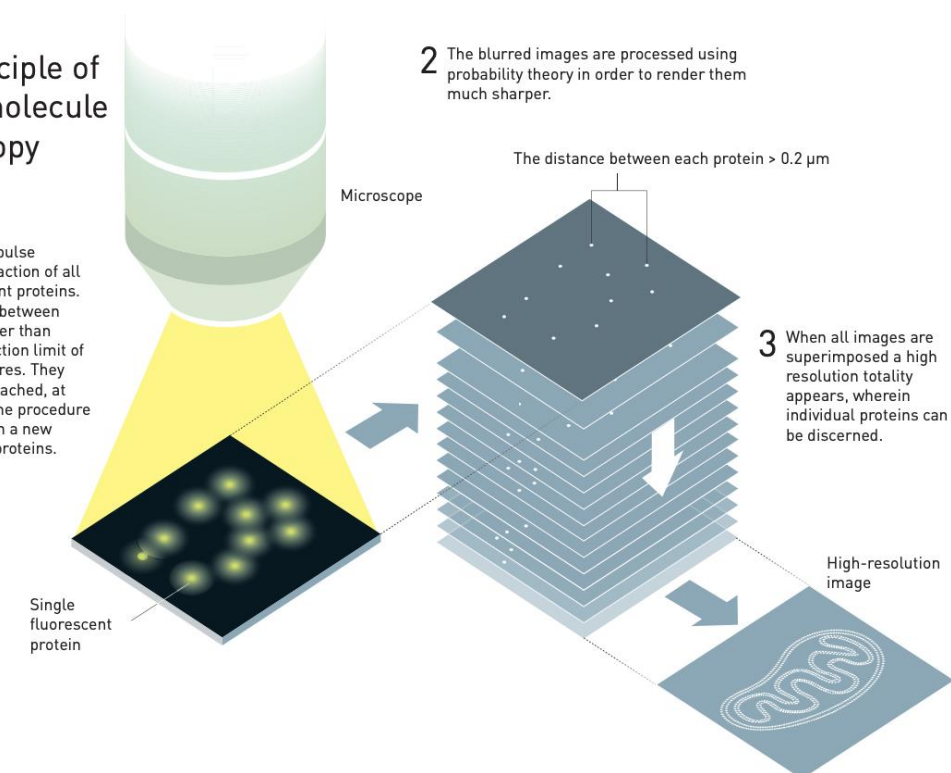
Figure 4

## The principle of single-molecule microscopy

1 A weak light pulse activates a fraction of all the fluorescent proteins. The distance between them is greater than Abbe's diffraction limit of 0.2 micrometres. They glow until bleached, at which point the procedure is repeated on a new subgroup of proteins.

2 The blurred images are processed using probability theory in order to render them much sharper.

3 When all images are superimposed a high resolution totality appears, wherein individual proteins can be discerned.



## Recent examples of applications of light to chemistry

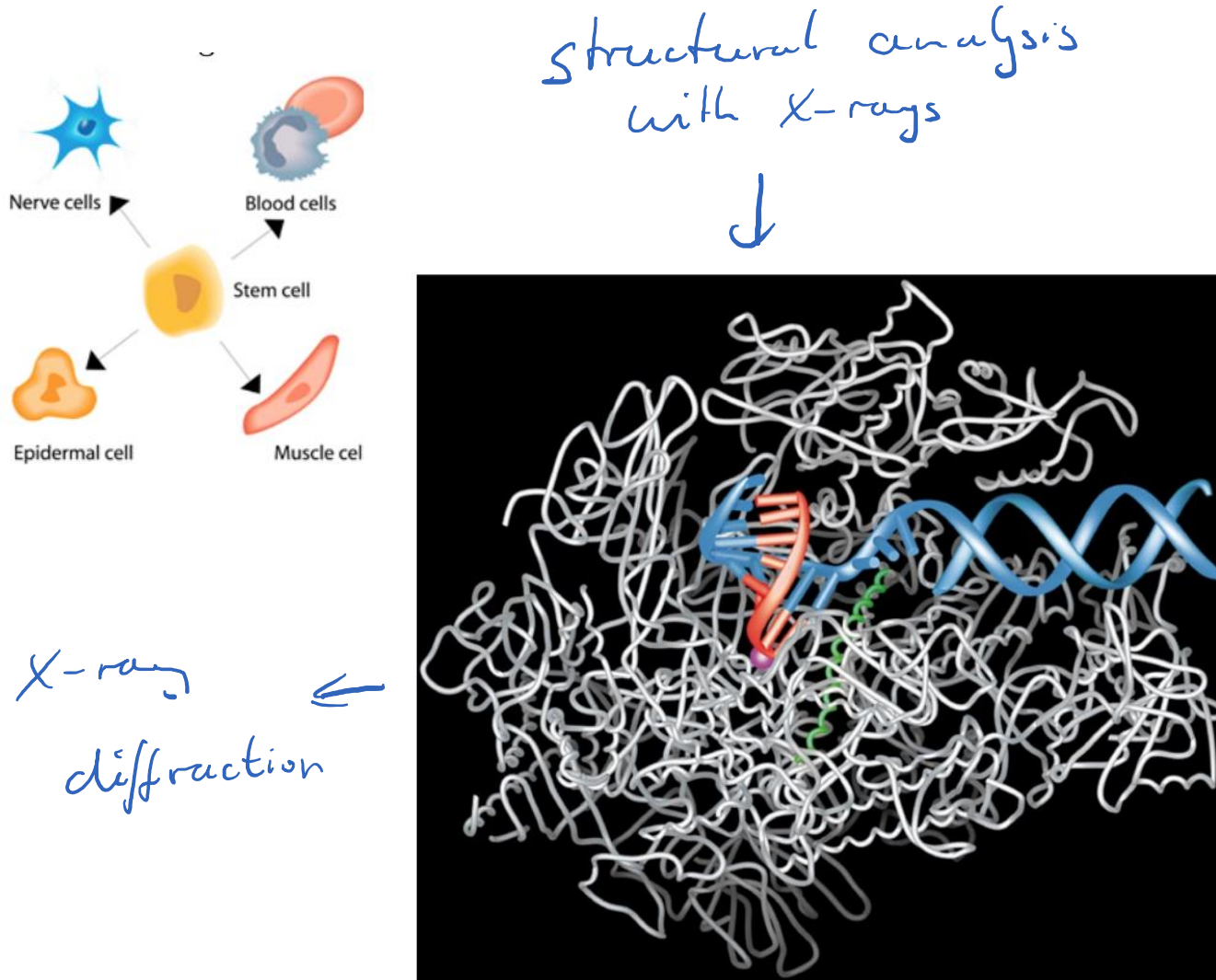


Figure 1. The transcription process as depicted by Roger Kornberg in 2001. RNA-polymerase in white, DNA-helix in blue and the growing RNA-strand in red.

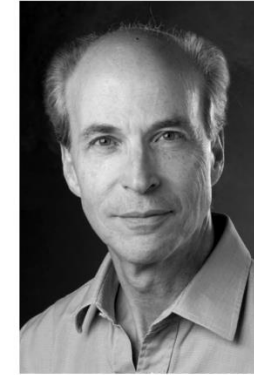
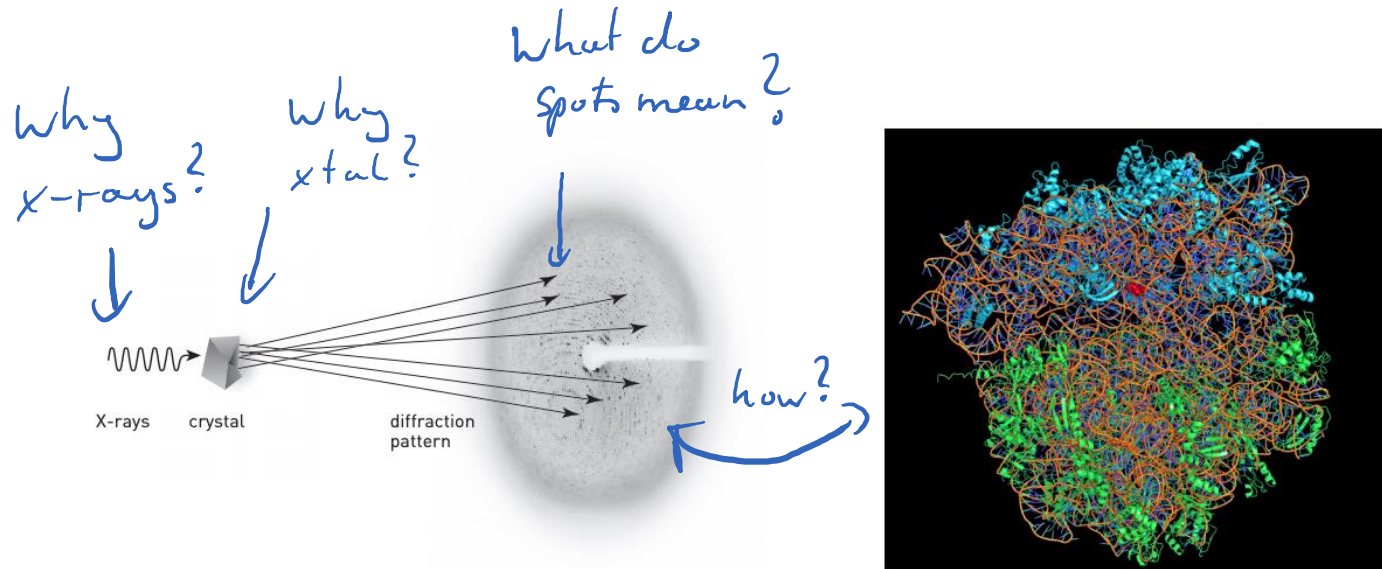


Photo: Stanford University  
Roger D. Kornberg  
Prize share: 1/1

This year's Nobel Prize in Chemistry is awarded to Roger D. Kornberg for his fundamental studies concerning **how the information stored in the genes is copied, and then transferred to those parts of the cells that produce proteins**. Kornberg was the first to create an actual picture of this process at the molecular level, in the important group of organisms called eukaryotes (which, as opposed to bacteria, have well-defined cell nuclei). Mammals like ourselves, as well as ordinary yeast, belong to this group of organisms.

## Recent examples of applications of light to chemistry



**Figure 4. X-ray crystallography.** The researchers create X-rays using synchrotrons, circular tunnels where electrons are accelerated to nearly the speed of light. When the rays hit the ribosome crystal they scatter, making millions of dots on a CCD detector. By analyzing this pattern, researchers can determine the position of each atom in the ribosome. Special software is used to visualize the ribosome (picture to the right).

At the beginning of the twentieth century, the chemical foundations for life were a mystery. Today we know how many of the most important processes function, all the way down to the atomic level. The 2009 Nobel Prize in Chemistry is awarded for the detailed mapping of the ribosome – the cell's own protein factory. The ribosome translates the passive DNA information into form and function.

## The Nobel Prize in Chemistry 2009



© The Nobel Foundation. Photo: U. Montan

Venkatraman  
Ramakrishnan

Prize share: 1/3



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Thomas A. Steitz

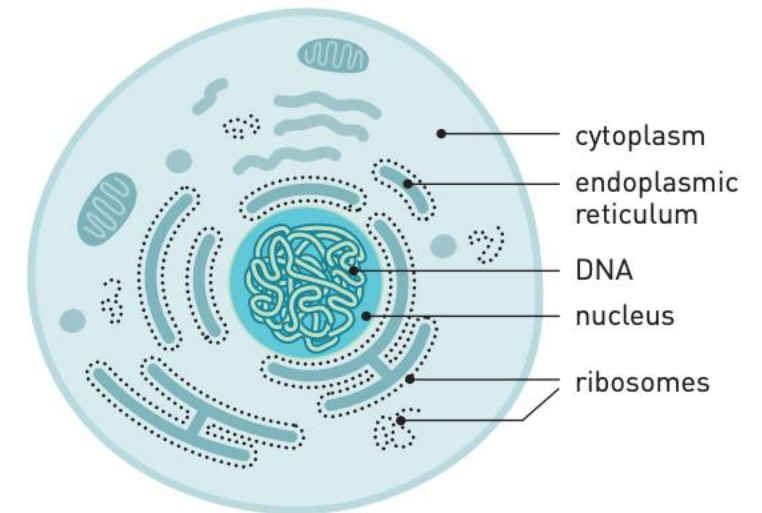
Prize share: 1/3



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Ada E. Yonath

Prize share: 1/3



# Recent examples of applications of light to chemistry

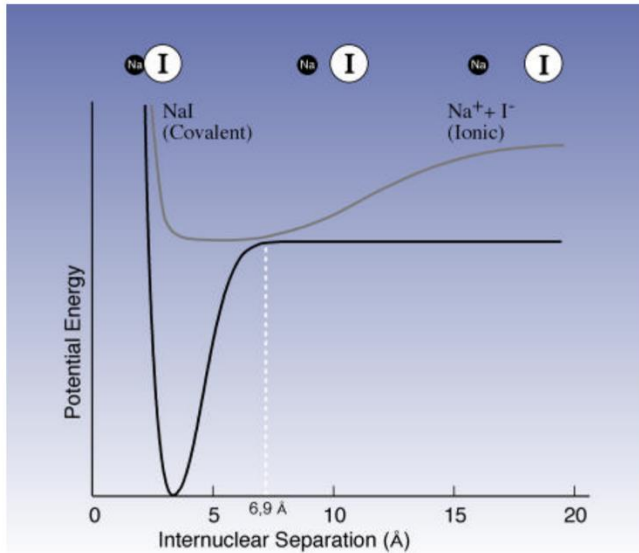


Fig. 1a) Potential energy curves showing the energies of ground state (bottom curve with deep minimum) and excited state (top curve) for NaI as function of the distance between the nuclei.

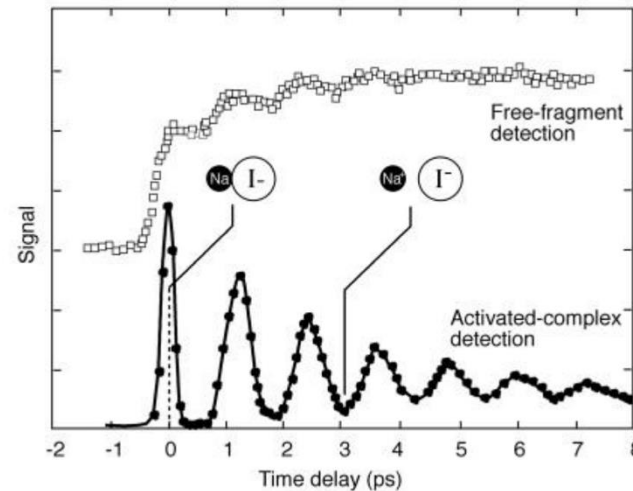
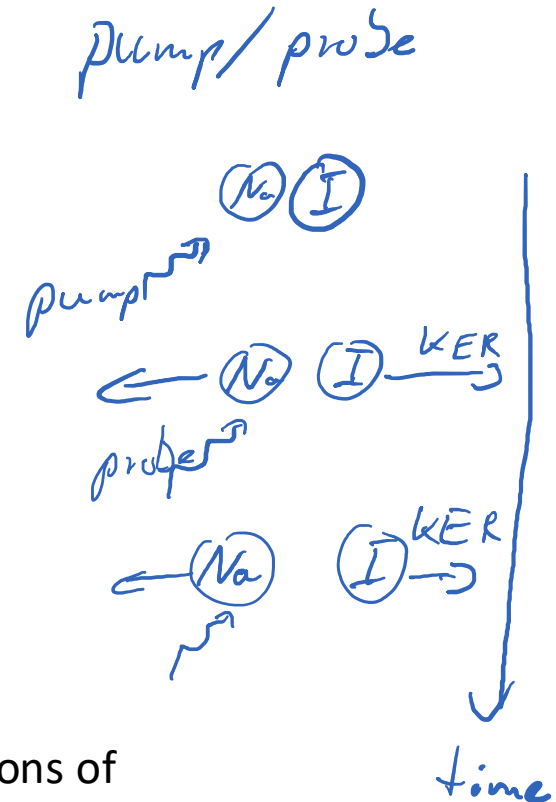


Fig. 1b) Experimental observations of coherent vibrations (so-called wave-packet motion) in femtosecond-excited NaI, on one hand manifested in terms of amount of activated complex  $[Na-I]^*$  at covalent (short) distance, on the other



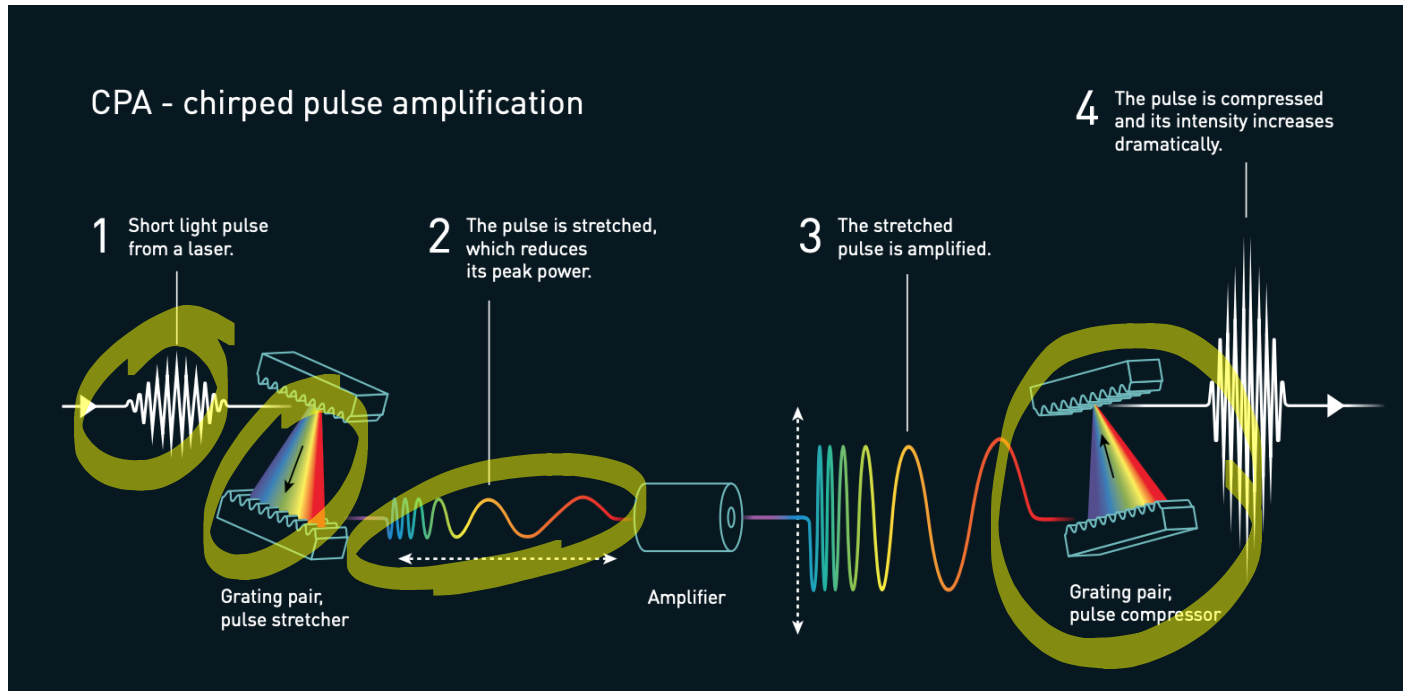
Photo from the Nobel Foundation archive.  
Ahmed H. Zewail  
Prize share: 1/1



KER -  
kinetic  
energy  
release

This year's Nobel Laureate, Professor Ahmed Zewail, is rewarded for his pioneering investigations of chemical reactions on the time-scale they really occur. This is the same timescale on which the atoms in the molecules vibrate, namely femtoseconds (1 fs = 10<sup>-15</sup> seconds). Only recently have developments in laser technology enabled us to study such rapid processes, using ultra-short laser flashes. Professor Zewail's contributions have brought about a revolution in chemistry, with consequences for many other fields of science, since this type of investigation allows us to understand and predict important processes.

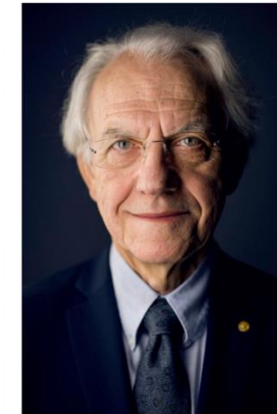
## Also in physics



## The Nobel Prize in Physics 2018



Ill. Niklas Elmehed. © Nobel Media  
**Arthur Ashkin**  
Prize share: 1/2



© Nobel Media AB. Photo: A. Mahmoud  
**Gérard Mourou**  
Prize share: 1/4



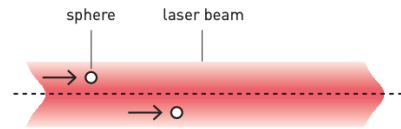
© Nobel Media AB. Photo: A. Mahmoud  
**Donna Strickland**  
Prize share: 1/4

→ gratings, pulses, short pulses, pulse stretching

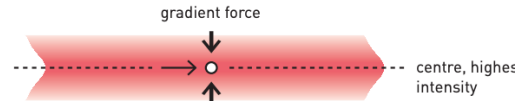
The inventions being honoured this year have **revolutionised laser physics**. Extremely small objects and incredibly fast processes now appear in a new light. Not only physics, **but also chemistry, biology and medicine** have gained precision instruments for use in basic research and practical applications. Arthur Ashkin invented optical tweezers that grab particles, atoms and molecules with their laser beam fingers. Viruses, bacteria and other living cells can be held too, and examined and manipulated without being damaged. Ashkin's optical tweezers have created entirely new opportunities for observing and controlling the machinery of life. Gérard Mourou and Donna Strickland paved the way towards the shortest and most intense laser pulses created by mankind. The technique they developed has opened up new areas of research and led to **broad industrial and medical applications; for example, millions of eye operations are performed every year with the sharpest of laser beams.**

## Also in physics

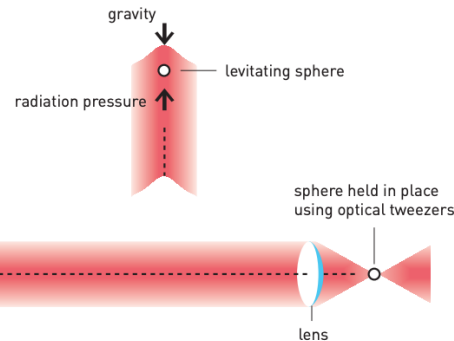
1 Small transparent spheres are set in motion when they are illuminated with laser light. Their speed corresponds to Ashkin's theoretical estimation, demonstrating that it really is radiation pressure pushing them.



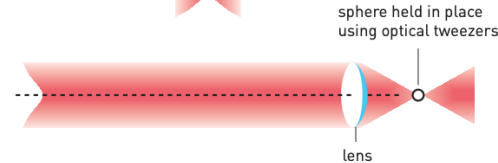
2 One unexpected effect was the gradient force that pushes the spheres towards the centre of the beam, where the light is most intense. This is because the intensity of the beam decreases outwards and the sum of all the forces pushing the spheres sends them towards its centre.



3 Ashkin makes the spheres levitate by pointing the laser beam upwards. The radiation pressure counteracts gravity.



4 The laser beam is focused with a lens. The light captures particles and even live bacteria and cells in these optical tweezers.



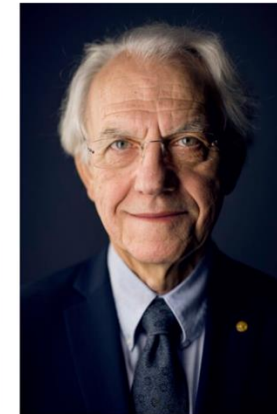
Optical tweezers:

<https://www.youtube.com/watch?v=ju6wENPtXu8>

## The Nobel Prize in Physics 2018



III. Niklas Elmehed. © Nobel Media  
**Arthur Ashkin**  
Prize share: 1/2



© Nobel Media AB. Photo: A. Mahmoud  
**Gérard Mourou**  
Prize share: 1/4



© Nobel Media AB. Photo: A. Mahmoud  
**Donna Strickland**  
Prize share: 1/4

The inventions being honoured this year have revolutionised laser physics. Extremely small objects and incredibly fast processes now appear in a new light. Not only physics, but also chemistry, biology and medicine have gained precision instruments for use in basic research and practical applications. **Arthur Ashkin invented optical tweezers that grab particles, atoms and molecules with their laser beam fingers. Viruses, bacteria and other living cells can be held too, and examined and manipulated without being damaged.** Ashkin's optical tweezers have created entirely **new opportunities for observing and controlling the machinery of life.** Gérard Mourou and Donna Strickland paved the way towards the shortest and most intense laser pulses created by mankind. The technique they developed has opened up new areas of research and led to broad industrial and medical applications; for example, millions of eye operations are performed every year with the sharpest of laser beams.

## Also in physics

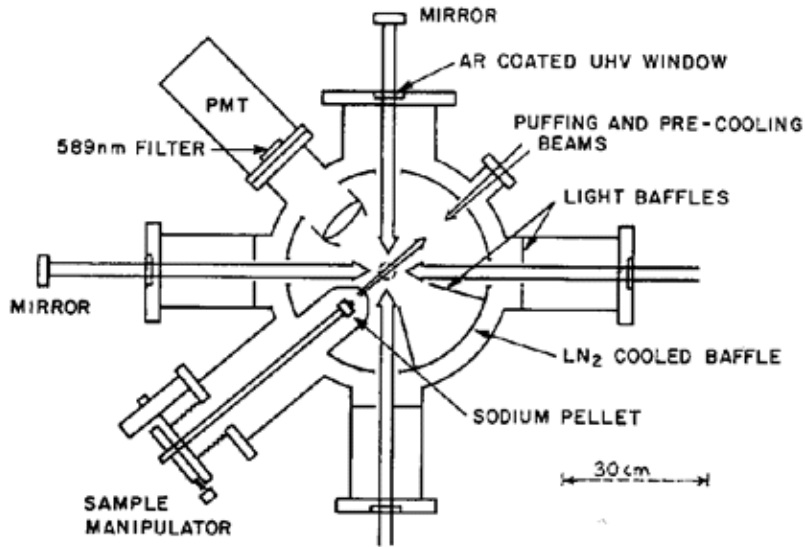


Photo from the Nobel Foundation archive.

Steven Chu

Prize share: 1/3



Photo from the Nobel Foundation archive.

Claude Cohen-Tannoudji



Photo from the Nobel Foundation archive.

William D. Phillips

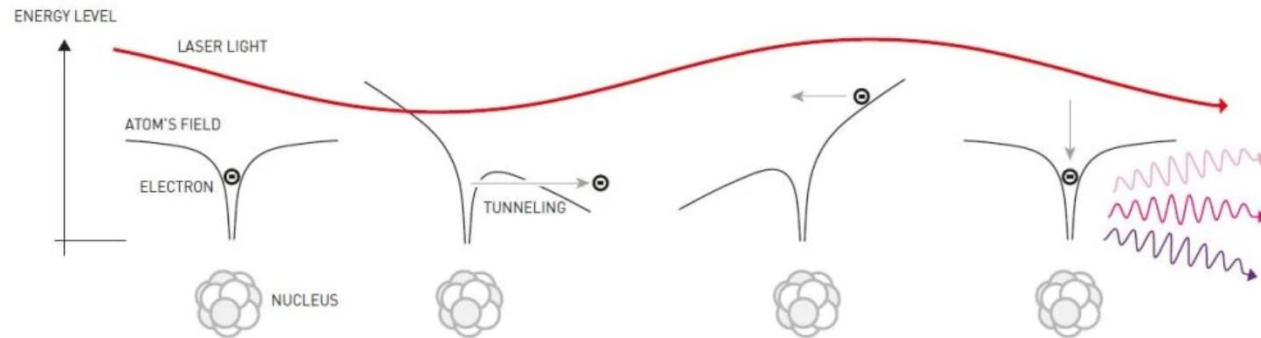
Prize share: 1/3

**Steven Chu, Claude Cohen-Tannoudji, and William D. Phillips** have developed methods of using laser light to cool gases to the  $\mu\text{K}$  temperature range and keeping the chilled atoms floating or captured in different kinds of “atom traps”. The laser light functions as a thick liquid, dubbed optical molasses, in which the atoms are slowed down. Individual atoms can be studied there with very great accuracy and their inner structure can be determined. As more and more atoms are captured in the same volume a thin gas forms, and its properties can be studied in detail. The new methods of investigation that the Nobel Laureates have developed have contributed greatly to increasing our knowledge of the interplay between radiation and matter. In particular, they have opened the way to a deeper understanding of the quantum-physical behaviour of gases at low temperatures. The methods may lead to the design of more precise atomic clocks for use in, e.g., space navigation and accurate determination of position. A start has also been made on the design of atomic interferometers with which, e.g., very precise measurements of gravitational forces can be made, and atomic lasers, which may be used in the future to manufacture very small electronic components.

## And most recent

### Laser light interacts with atoms in a gas

Experiments that created overtones in laser light led to the discovery of the mechanism that causes them. How does it work?



- 1 An electron that is bound to an atom's nucleus cannot normally leave its atom; it does not have enough energy to lift itself out of the well created by the atom's electrical field.
- 2 The atom's field is distorted when it is affected by the laser pulse. When the electron is only held by a narrow barrier, quantum mechanics allow it to tunnel out and escape.
- 3 The free electron is still affected by the laser field and gains some extra energy. When the field turns and changes direction, the electron is pulled back in the direction it came from.
- 4 To reattach to the atom's nucleus, the electron must rid itself of the extra energy it gained during its journey. This is emitted as an ultraviolet flash, the wavelength of which is linked to that of the laser field, and differs depending on how far the electron moved.



© Nobel Prize Outreach. Photo: Clément Morin  
**Pierre Agostini**  
Prize share: 1/3



© Nobel Prize Outreach. Photo: Clément Morin  
**Ferenc Krausz**  
Prize share: 1/3



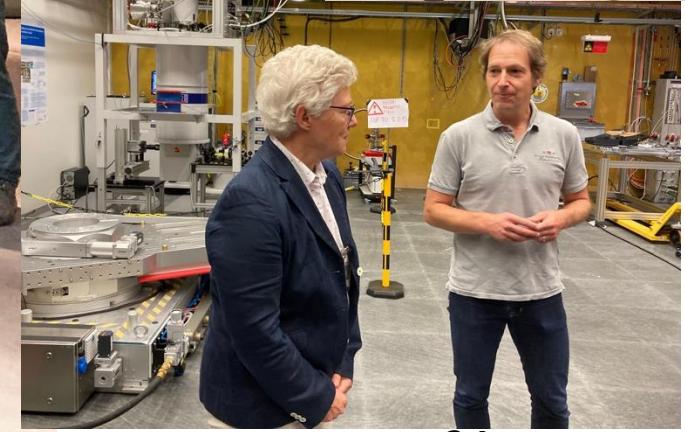
© Nobel Prize Outreach. Photo: Clément Morin  
**Anne L'Huillier**  
Prize share: 1/3

→ High harmonic generation

→ XUV pulses matched to questions in chemistry / molecular energy transitions  
→ sub-femtosecond / attosecond pulses

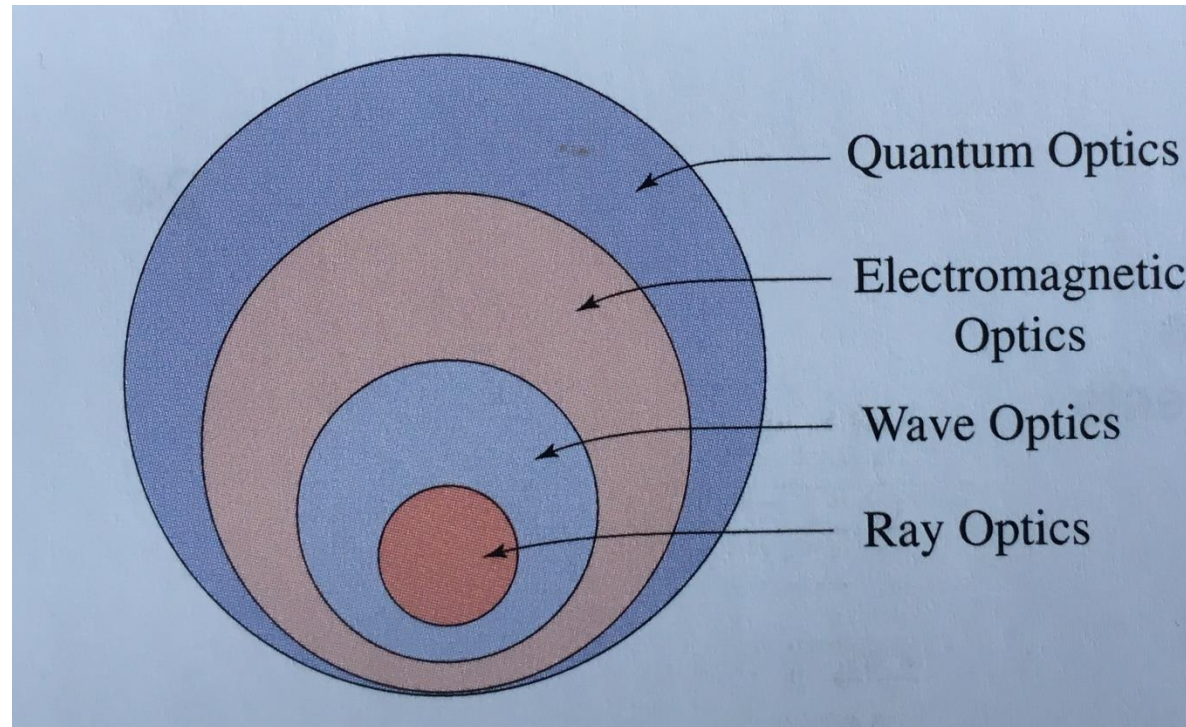
The three Nobel Laureates in Physics 2023 are being recognised for their experiments, which have given humanity **new tools for exploring the world of electrons inside atoms and molecules**. Pierre Agostini, Ferenc Krausz and Anne L'Huillier have demonstrated a way to **create extremely short pulses of light that can be used to measure the rapid processes in which electrons move or change energy**.

## Last week at SwissFEL

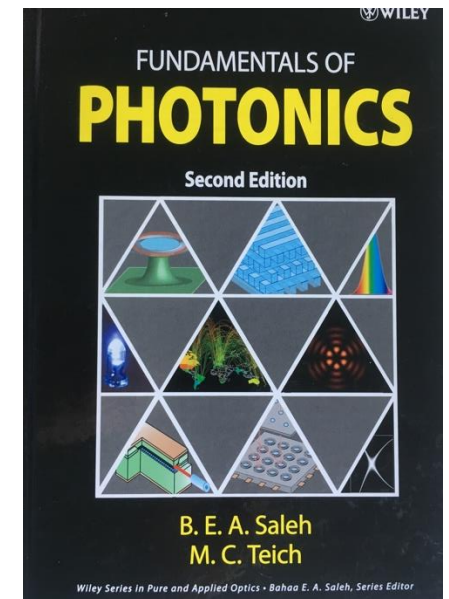


Which are your favorite examples?

Much exciting science – but you need to know some basics



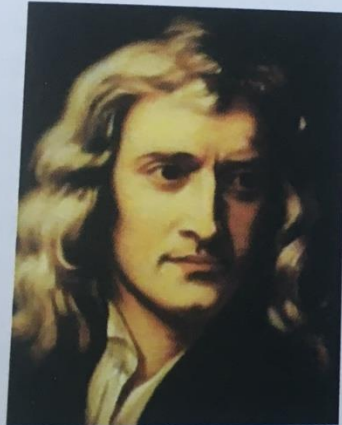
Main source for next topics



# Ray optics

- Geometrical optics
- Image formation
- Location and direction of light rays

Historical perspective but also daily experience



**Sir Isaac Newton (1642–1727)** set forth a theory of optics in which light emissions consist of collections of corpuscles that propagate rectilinearly.



**Pierre de Fermat (1601–1665)** enunciated the principle that light travels along the path of least time.

# Postulate of ray optics

➤ Light travels in form of rays

➤ Rays are emitted by a light source and can be observed when they reach an optical detector

➤ An optical medium is characterized by a quantity  $n \geq 1$  called refractive index with

➤  $n = c_0/c$  and  $c$  = speed of light  $\rightarrow$  inside a medium  $c$ ,  $c_0$  - speed of light

➤ Time for traveling a distance  $d$  takes:  $t = \frac{d}{c} = n \frac{d}{c_0}$

➤  $nd$  is called the optical path length  $n \cdot d$

➤ In an inhomogeneous medium the refractive index  $n(r)$  depends on  $r(x,y,z)$

➤ Optical path length expressed as integral:  $\int_A^B n(r) ds$

➤ Time to travel from A to B is proportional to the optical path length

## Fermat's principle

Optical rays traveling between two points A and B follow a path such that the time of travel (that is optical path length) between the two points is at an extremum (usually minimum)

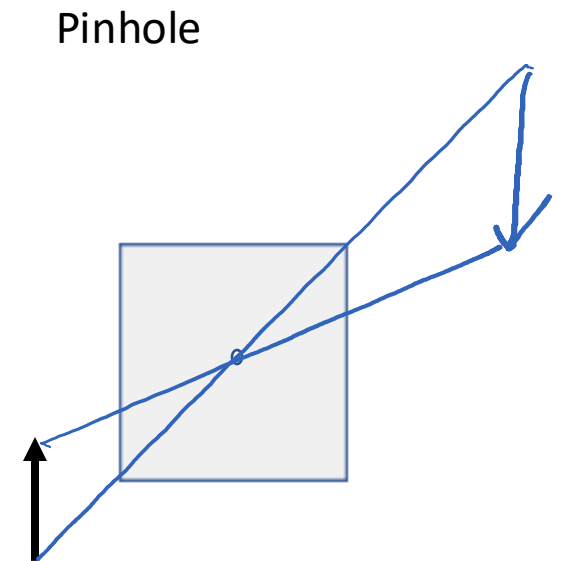
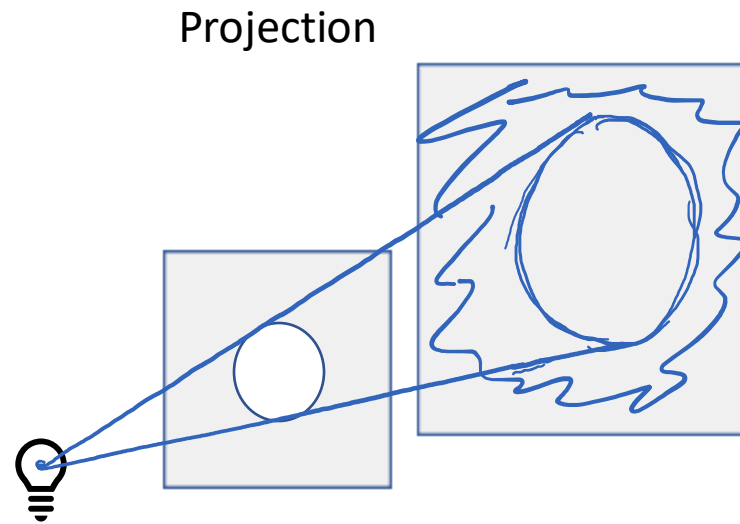
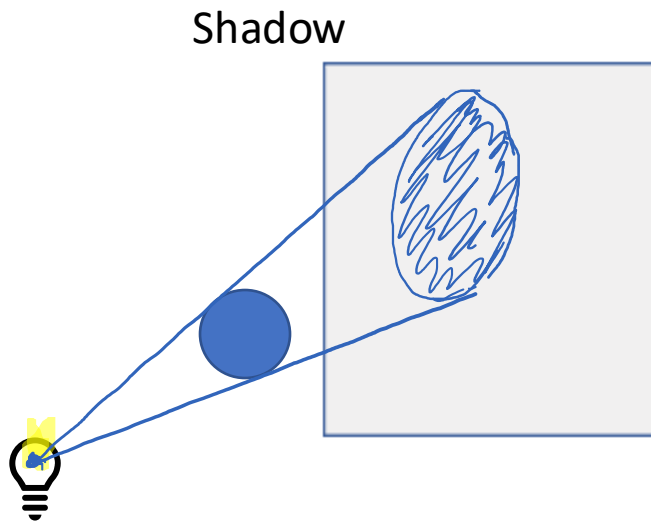
$$\delta \int_A^B n_{cr} ds = 0$$

In other words: Light travels along the path of least time

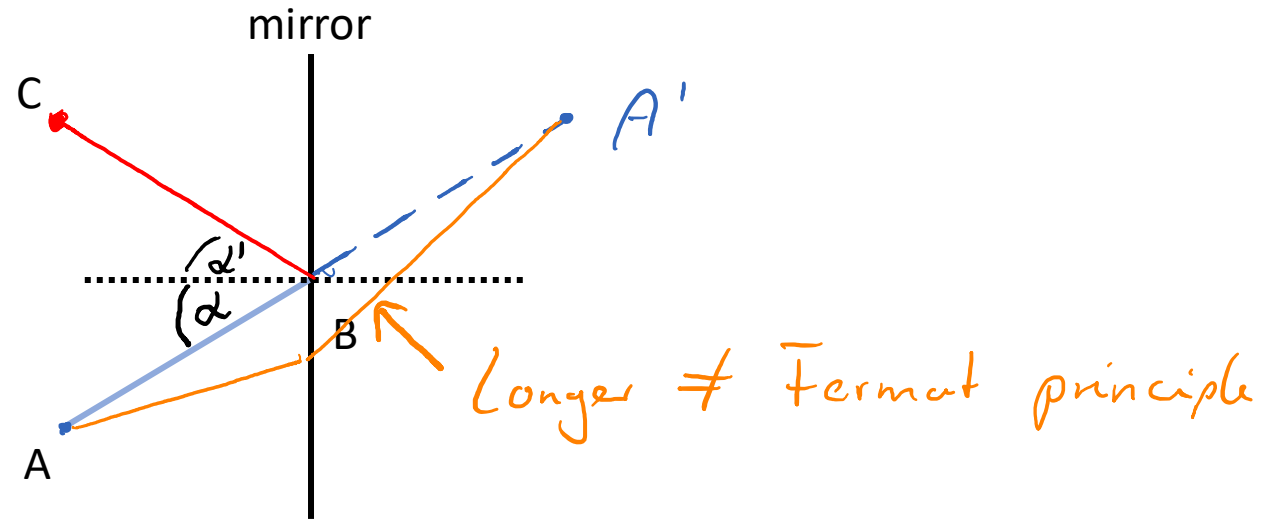
In homogenous media this results in Hero's principle

Hero's principle: The path of minimal time is also the **path of minimal distance**.

Or in other words: Light travels **in straight lines**. Lets try it, draw an image of



## Reflection from a mirror



The reflection lays in the plane of incidence.

The angle of the reflection  $\alpha'$  the angle of incidence  $\alpha$

## Snell's law – reflection and refraction at the boundary of two media

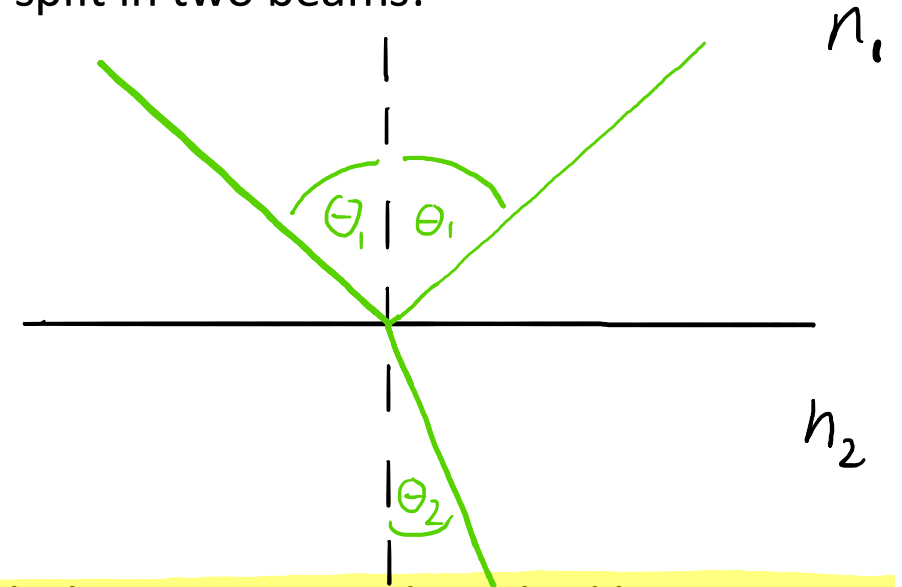
At the boundary of two media with  $n_1$  and  $n_2$  the incident ray is split in two beams:  
a *reflected* and a *refracted* beam

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

Snell's law

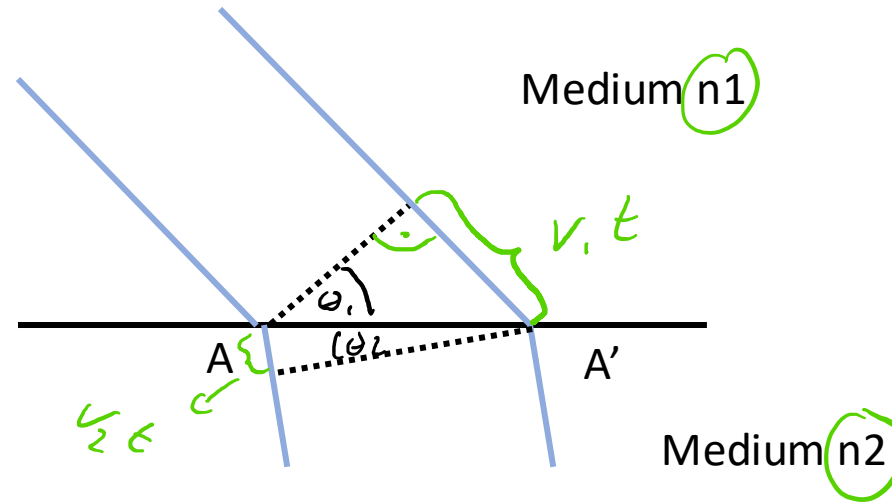
or

$$\frac{n_1}{n_2} = \frac{\sin \theta_2}{\sin \theta_1}$$



Important note: the proportion of the reflected and refracted light beams are *not* described by Ray optics

## Snell's law based on what we have learned so far



- Same time means same distance travelled,  $t = \text{const}$

$$\sin \theta_1 = \frac{v_1 t}{AA'}, \quad \sin \theta_2 = \frac{v_2 t}{AA'}$$

- From geometry:  $\sin$

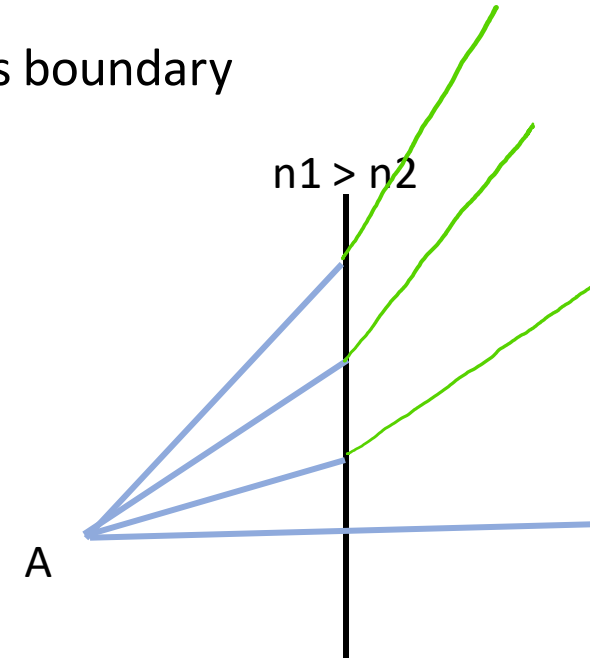
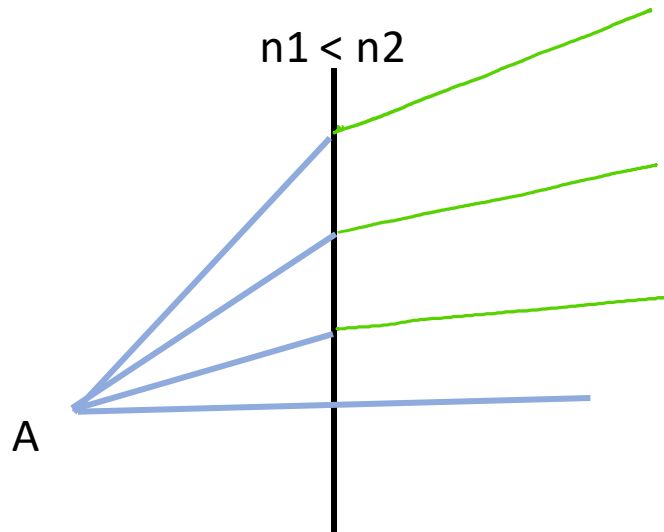
$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{v_1 t}{v_2 t} = \frac{n_2}{n_1} \quad \Bigg| \quad v_1 = \frac{c_0}{n_1} \quad \& \quad v_2 = \frac{c_0}{n_2}$$

- Results in Snell's law

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

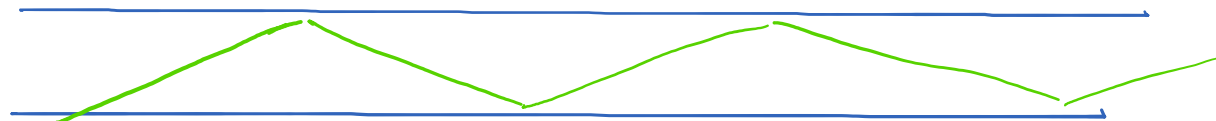
# Optical boundaries

- External refraction  $n_1 < n_2$  – refracted ray bends away
- Internal refraction  $n_1 > n_2$  – refracted light bends towards boundary



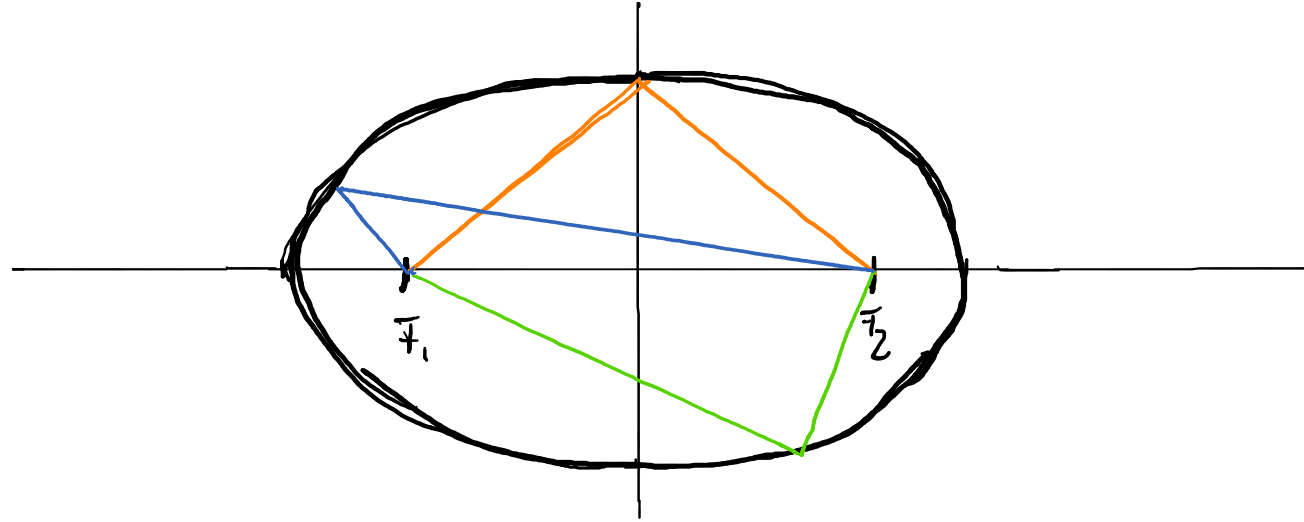
- Total internal reflection
- Use for optical fibers

$$\frac{n_2}{n_1} = \frac{\sin \theta_1}{\sin \theta_2} \left\{ \begin{array}{l} \longleftrightarrow 90^\circ \rightarrow \infty \end{array} \right\} \rightarrow \infty$$

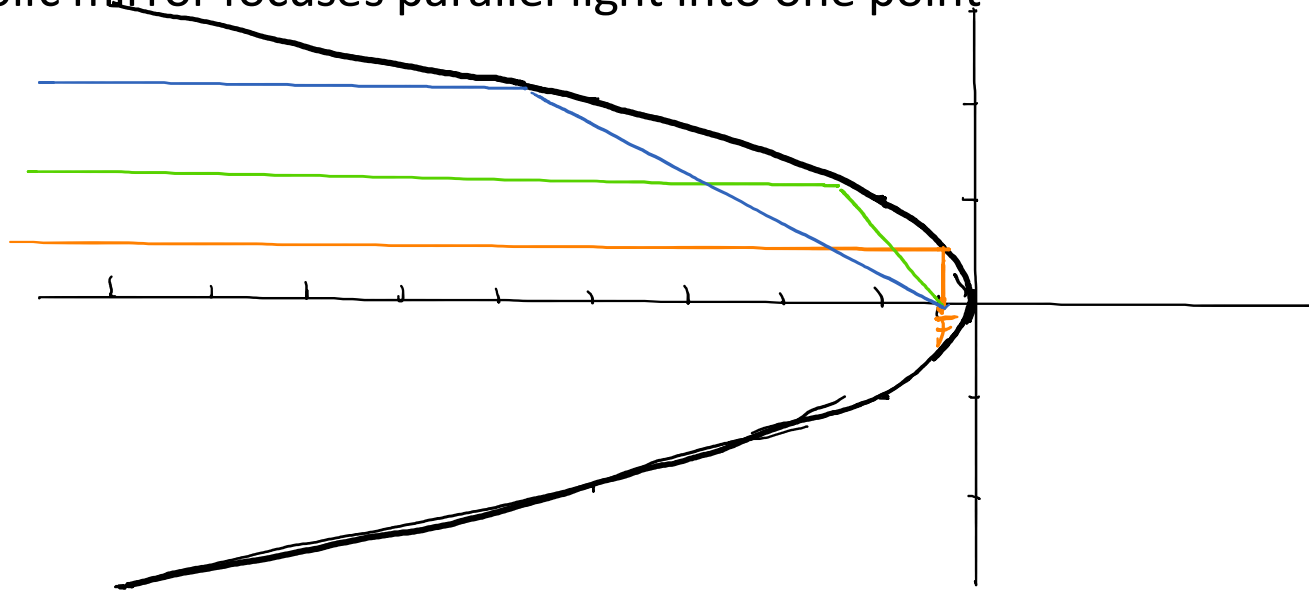


## Some optical components

- Ellipse – elliptical mirror reflects all light emitted in one focal point into another focal point



- Parabola – a parabolic mirror focuses parallel light into one point

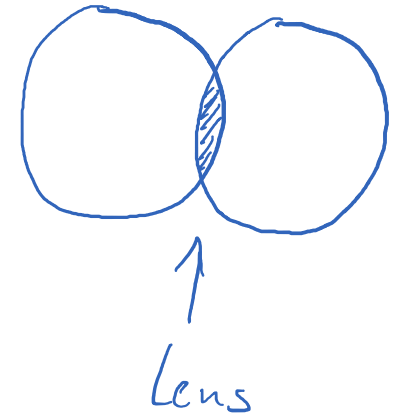


## Spherical mirror

- Most common mirror, easy to fabricate
- Neither imaging properties of ellipse nor focusing properties of parabola
- Parallel beams meet at different points
- But it is still useful, see exercise

## Exercise question

- Where is the focal point of a spherical mirror?
- Under which conditions is an image formed?
- Where is the image formed?
- Construct the properties of a spherical mirrors with ray optics.



That is the new material for today

Next week: from waves to beams

Homework: read and digest Nobel summary of Zewail as well as Mourou and Strickland as well as Betzig and Hell and Moerner

## Exercise

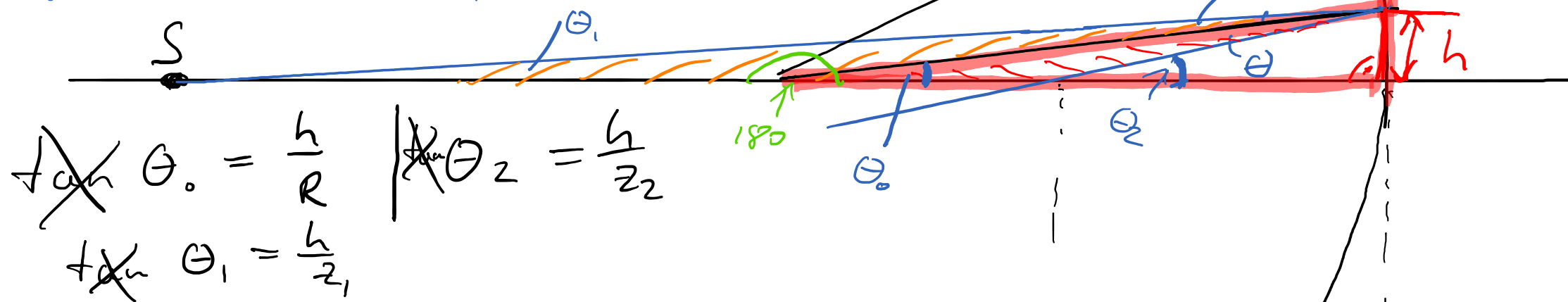
- Where is the focal point of a spherical mirror?
- Under which conditions is an image formed?
- Where is the image formed?
- Construct the properties of a spherical mirrors with ray optics.

$$\triangle \rightarrow \alpha + \beta + \gamma = 180$$

$$\left. \begin{aligned} \theta_1 + \theta + 180 - \theta_0 &= 180 \\ \theta_0 + \theta + 180 - \theta_2 &= 180 \end{aligned} \right\} \begin{aligned} \theta &= \theta_0 - \theta_1 \\ \theta &= \theta_2 - \theta_0 \end{aligned} \left. \vphantom{\begin{aligned} \theta &= \theta_0 - \theta_1 \\ \theta &= \theta_2 - \theta_0 \end{aligned}} \right\} 2\theta_0 = \theta_2 + \theta_1$$

$$\tan \alpha = \alpha$$

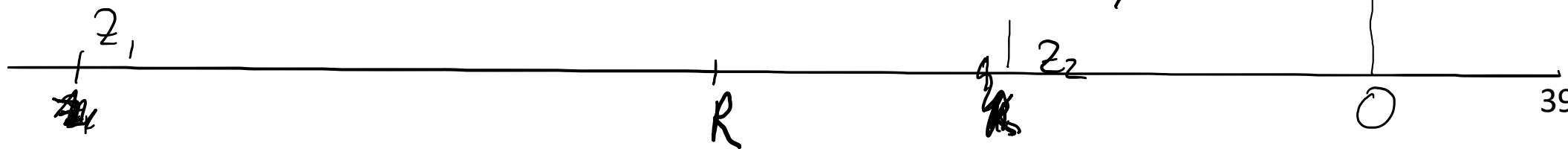
Small  $\alpha$



$$\cancel{\tan \theta_0 = \frac{h}{R}} \quad \cancel{\tan \theta_2 = \frac{h}{z_2}}$$

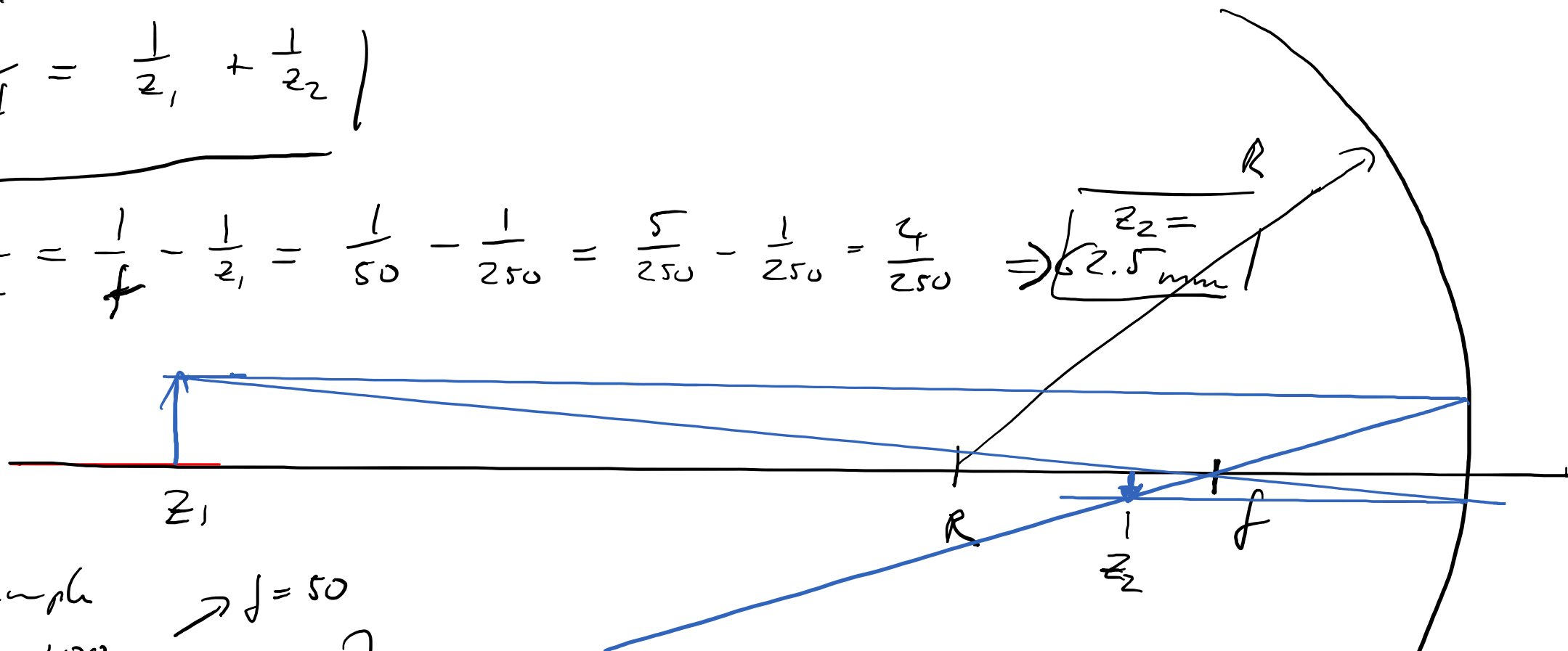
$$\cancel{\tan \theta_1 = \frac{h}{z_1}}$$

$$\Rightarrow \frac{2}{R} = \frac{1}{z_2} + \frac{1}{z_1} \left\} \frac{2}{R} = \frac{1}{z_2} + \frac{1}{z_1} \xrightarrow{z_1 \rightarrow \infty} \boxed{\frac{2}{R} = \frac{1}{z_2}} \rightarrow \boxed{f = \frac{R}{2}}$$



$$\boxed{\frac{1}{f} = \frac{1}{z_1} + \frac{1}{z_2}}$$

$$\frac{1}{z_2} = \frac{1}{f} - \frac{1}{z_1} = \frac{1}{50} - \frac{1}{250} = \frac{5}{250} - \frac{1}{250} = \frac{4}{250} \Rightarrow \boxed{z_2 = 62.5 \text{ mm}}$$



Example  $f = 50$

$R = 100 \text{ mm}$

object 60 mm

distance 250 mm  
( $z_1$ )

Where is  
image?

↓  
 $z_2$

Magnification  $M = \frac{z_1}{z_2} = \frac{250}{62.5} = \frac{1}{4} = 41 \frac{1}{4}$