

## Describing many-particle systems - part II

### Light absorption

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2015, October 21

### Reminder: Boltzmann distribution



Ludwig Eduard Boltzmann  
1844-1906, Austrian physicist

$N$  distinguishable independent particles at thermal equilibrium,  $T \neq 0$  in a closed system, exposed to a force field

$\varepsilon_i$  possible energy status for one particle  
 $n_i$  number of particles having  $\varepsilon_i$  energies

$$E = \sum_j n_j \varepsilon_j \quad N = \sum_j n_j$$

### Boltzmann distribution function

$$\frac{n_k}{n_j} = e^{-\frac{\varepsilon_k - \varepsilon_j}{kT}} = e^{-\frac{\Delta \varepsilon}{kT}}$$

Boltzmann factor

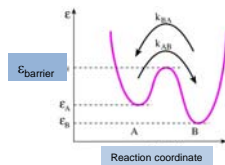
Valid for any (j,k) combinations of energy levels



The particles are allowed to have a temperature dependent broad variety of energies according to a strict law of population

### Boltzmann distribution - more examples (see textbook)

#### 3. Equilibrium rate of chemical reactions



Reaction :  $A \rightleftharpoons B$

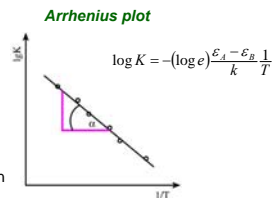
The  $k_{AB}$  and  $k_{BA}$  rates are proportional to the number of reactants which are higher in energy, reaching the top of the barrier

$$k_{AB} = \text{const} \times e^{-\frac{\varepsilon_{\text{barrier}} - \varepsilon_A}{kT}}$$

$$k_{BA} = \text{const} \times e^{-\frac{\varepsilon_{\text{barrier}} - \varepsilon_B}{kT}}$$

$$K = \frac{k_{BA}}{k_{AB}} = e^{-\frac{\varepsilon_A - \varepsilon_B}{kT}}$$

Experimental determination of the energy of activation



#### 4. Barometric formula

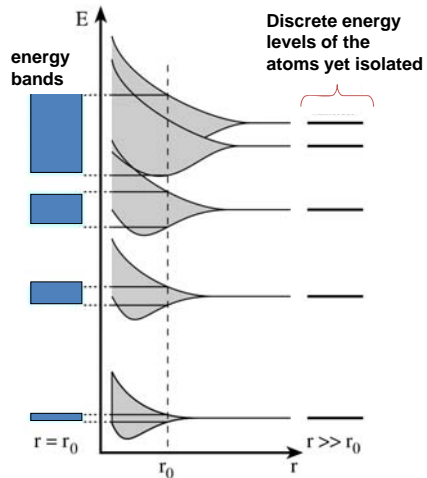
Density of air in the atmosphere decreases with the altitude ( $h$ ) by the formula:

$$\frac{\rho(h)}{\rho(0)} = e^{-\frac{mgh}{kT}}$$

$m$  average mass of particles in the air  
 $g$  gravitational acceleration

The interaction of particles in ordered systems changes the **electronic energy levels**

## Crystalline materials

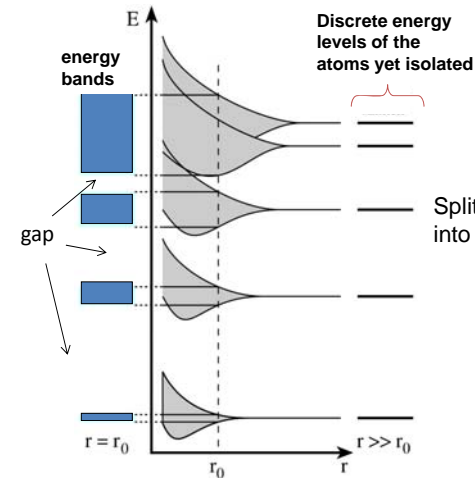


$$N \sim 10^{23}$$

$N$  no. of isolated atoms with discrete energy levels change their electronic states when they interact to form crystalline state with bond distance  $r_0$ .

Splitting of discrete levels into  $N$  new levels results in continuous ranges : **energy bands**

Interaction of ordered atoms changes the electronic energy levels  
discrete energy levels  $\rightarrow$  continuous ranges of energies (bands) separated by forbidden states (energy gaps)



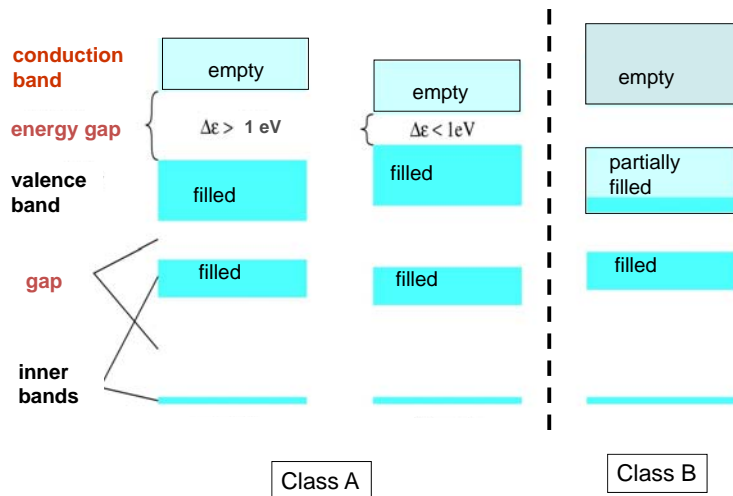
Example: solid state Na  
 $1s^2 2s^2 2p^6 3s^1$

$$2(2l+1)N = \text{number of electrons in one band}$$

3p	0
3s	$N$
2p	$6N$
2s	$2N$
1s	$2N$

The fourth level is only half-filled

The physical (chemical) properties depend on the energetic relations of highest filled and lowest empty electronic states  $\rightarrow$  **three important classes of materials**



Class A - materials

depending on the magnitude of the energy gap

Class A1

Class A2

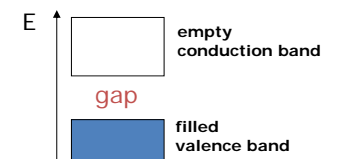
Why?

$$\frac{n_{cond}}{n_{valence}} = e^{-\frac{\Delta\epsilon}{kT}}$$

the relation of  $\Delta\epsilon = E_{gap}$  and  $kT$  determines whether the gap energy can be overcome by Boltzmann distribution

$$kT \sim 0.023 \text{ eV} \quad T=300 \text{ K},$$

$k=1.38 \times 10^{-23} \text{ J/K}$  Boltzmann constant



## Class A1

$$E_{gap} \gg 1\text{eV}$$

**Insulators:  $E_{gap}$  is large**

e.g. diamond  $E_{gap} = 5.4\text{ eV}$

$$\frac{n_{cond}}{n_{val}} = e^{-\frac{5.4}{0.023}} = e^{-235} = 0$$

- No electric conductivity (dielectric break-down:  $\sim V/\text{bond} \rightarrow 10^{10}\text{ V/m}$ )
- No photon absorption in the **VIS range**  $\rightarrow$  **transparency**
- UV photons may be absorbed, IR: excitation of lattice vibrations

## Class A2

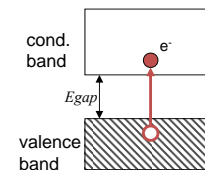
$$E_{gap} \leq 1\text{eV}$$

**$E_{gap}$  is small - intrinsic semiconductors**

Non-transparent crystalline materials

Reasonable number of thermally excited electrons in the conduction band

	$E_g\text{ (eV)}$	
Si	1.1	$\frac{n_{cond}}{n_{val}} = e^{-\frac{0.75}{0.023}} = e^{-33} = 7 \cdot 10^{-15}$
Ge	0.75	$n_{val} \approx 6 \cdot 10^{23} \Rightarrow n_{cond} \approx 4 \cdot 10^8 \text{ /cm}^3$



**n - type conductivity (electron conduction)**  $\sigma \approx e^{-\frac{E_{gap}}{2kT}}$

**p - type conductivity (electron-hole: + charge conduction)**

**Two kinds of charge carriers**

## Class A2

**intrinsic semiconductors**

$$\sigma = \text{const} * e^{-\frac{E_{gap}}{2kT}}$$

Slightly depends on T

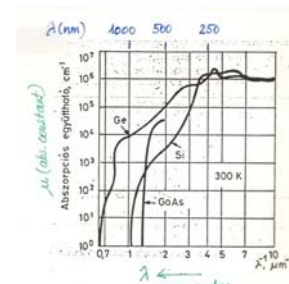
Equilibrium: generation and recombination of charge carriers is of equal probability  
 $p(\text{recombination}) \sim n^2$ ,  $p(\text{generation}) \sim \text{Boltzmann factor}$

**Specific conductivity is increased by temperature increase**  
 **$\rightarrow$  thermoresistors**

Optical properties: non-transparency in the VIS range

$$hf_{VIS} > E_{gap}$$

Photon absorption induces conductivity  
 **$\rightarrow$  photodetectors**



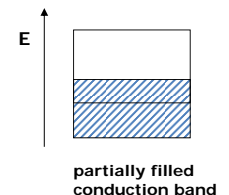
## Class B

**Metals :no gap**

e.g. 1-valence and 2-valence metals Na, Mg, Cu..

	Cu	Si	T=293 K
$n(\text{charge})/\text{m}^3$	$9 \cdot 10^{28}$	$1 \cdot 10^{16}$	
specific resistance (Ohmxm)	$2 \cdot 10^{-8}$	$3 \cdot 10^3$	

**high electric conductivity**



**Energy absorption is possible within the partially filled highest energy band**

-Electrons conduct electricity

-Optical non-transparency

$$\sigma \approx \frac{1}{T}$$

Specific conductivity decreases with T-increase

**semiconductors**

## Class A2\*\*

## doped semiconductors

**Doping:** incorporation of a second component (dopant) into the crystal lattice of an intrinsic semiconductor (host) in a small amount

$$\frac{N_{\text{host}}}{N_{\text{dopant}}} \approx 10^6$$

→ **Dopant atoms are isolated in the crystal matrix**

**Idea:** properly selected **dopant may reduce  $E_{\text{gap}}$** , thus increasing the number of thermally excited charge carriers : electrons or electron-holes

Two combinations:

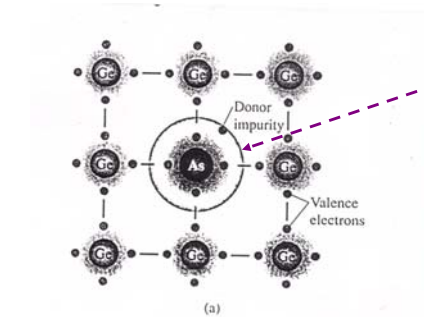
-4-valent host combined with 5-valent dopant → **n-type** doped semiconductor

-4-valent host combined with 3-valent dopant → **p-type** doped semiconductor

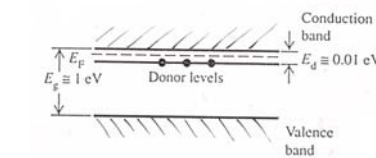
**Hosts: Ge, Si**

**Dopants: 5-valent : P, As, Bi**  
**3-valent : B, Al, Ga, In**

4-valence Ge crystal lattice doped with 5-valence As atoms

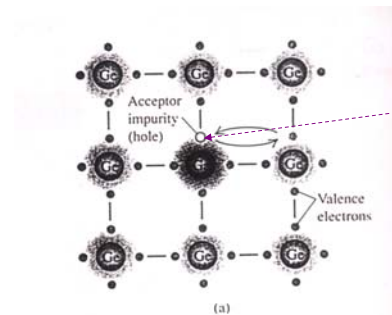


Loosely bound fifth electron can be easily involved in conduction  
→ **n-type conduction**

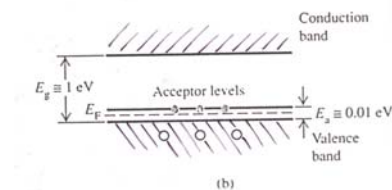


Donor level exists only at impurities. These electrons can not be moved by electric field. But, these can be raised into the conduction band by a low energy-surplus.

Doping 4 valence Ge crystal with 3 valence Ga

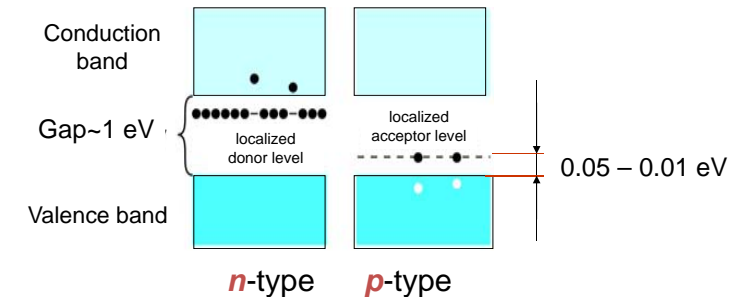


One electron is missing at Ga to form covalent bond with one Ge neighbor  
→ it can easily bind electrons from Ge-s  
→ **p-type conductivity**



Acceptor level exists only at the isolated impurity atoms, but the electron-hole can diffuse among the Ge-valence electrons

## Summary: n-type and p-type conduction

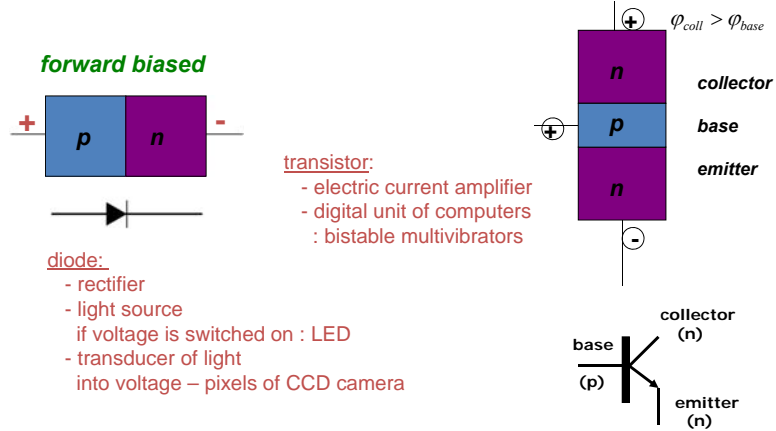


**electrons** thermally excited from the donor level of impurity conduct electricity

**electrons** thermally excited to the acceptor level of impurity are localized, but **electron-holes** conduct electricity

## diode and transistor:

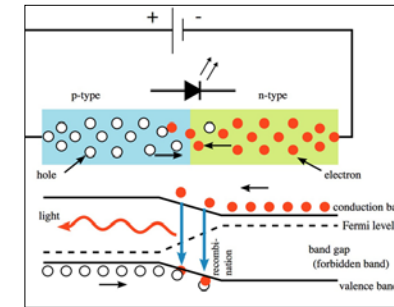
constructed from n- and p- type doped semiconductors



### diode:

- rectifier
- light source
- if voltage is switched on : LED
- transducer of light into voltage – pixels of CCD camera

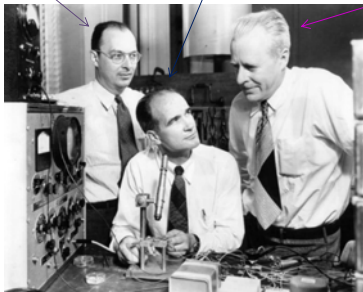
## Most modern light source: LED



Recombination of electrons and holes produces light

## 1956 - Nobel price in physics for the realization of the transistor

John Bardeen, William Shockley and Walter Brattain at Bell Labs, 1948.



**John Bardeen**  
II. Nobel 1972  
Theory of superconductivity



**Walter Brattain**  
Extremely talented  
experimental physicist

## 2014 – Nobel price in physics for the realization of the blue LED

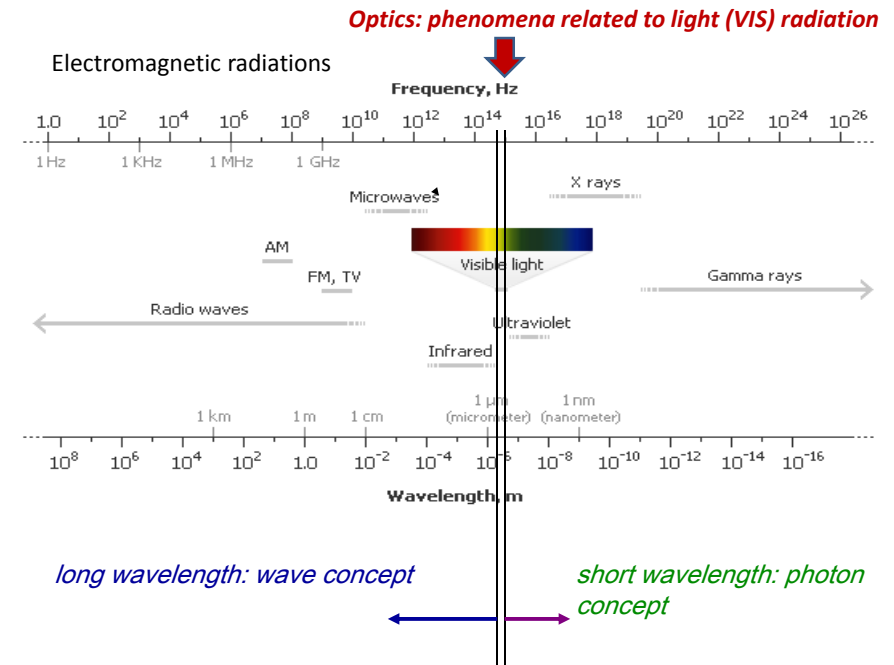
Isamu Akasaki , Shuji Nakamura, Hiroshi Amano ,



LED: Light Emitting Diode



## New chapter: back to light..... Light interaction with materials



### Light in interaction with materials

Two models for the interpretation of light phenomena

- wave description
- photon description

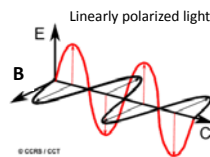


$$E_{\text{photon}} = hf$$

$$E = E_{\text{max}} \cdot \sin \left( 2\pi \frac{t}{T} + 2\pi \frac{x}{\lambda} + \Phi \right)$$

$$B = B_{\text{max}} \cdot \sin \left( 2\pi \frac{t}{T} + 2\pi \frac{x}{\lambda} + \Phi \right)$$

Amplitude



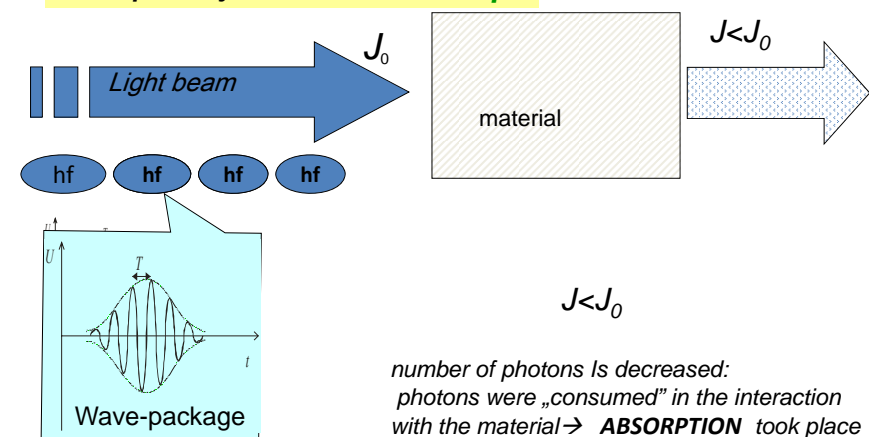
- Parameters of light :
- wavelength  $\lambda$
  - frequency  $f=1/T$
  - phase  $\phi$
  - intensity of light beam  $\propto \text{Amplitude}^2$
  - direction of vectors  $\mathbf{E}$  and  $\mathbf{B}$
  - direction of energy propagation

Interaction with materials  $\rightarrow$  change in the parameters of light beam

**Next: discussing the basics and description of light INTENSITY changes --- ATTENUATION OF LIGHT INTENSITY**

### ATTENUATION OF LIGHT INTENSITY by material interactions

Description by the **Photon-concept**

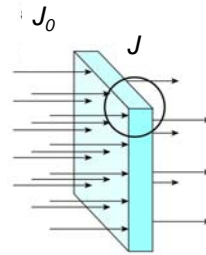


ABSORPTION  $\rightarrow J < J_0$

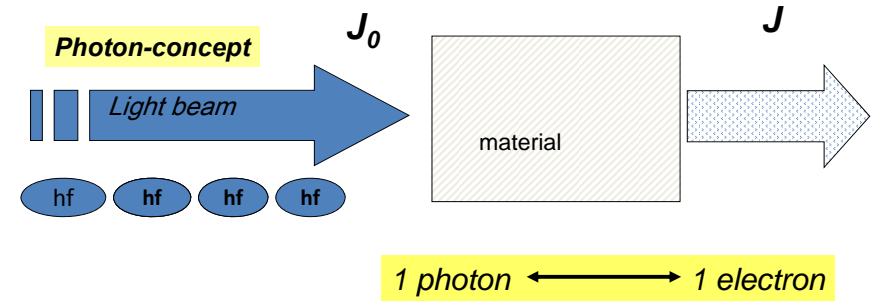
number of photons in  $J$  is smaller than in  $J_0$

$$P = \frac{\Delta E}{\Delta t} = \frac{\Delta N \cdot hf}{\Delta t}$$

$$J = \frac{\Delta P}{\Delta A} \quad J \left[ \frac{W}{m^2} \right]$$



photons became „consumed” in the interaction with the material



The interaction partner of the light photon is the electron.

How can the electrons use the  $E_{\text{photon}}$  of light? 1.5 – 3 eV?

Are they „allowed” to have higher energies?

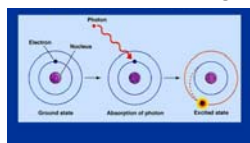
## Interaction of light with classes of materials

One electron can consume  $E_{\text{photon}}$  if it raises its energy to an „allowed” (existing) higher energy level

- within the nuclear bondages  $\rightarrow$  photo-**excitation**
- in the free electron states  $\rightarrow$  photo-**ionization**

### Schematics for electronic **excitation** by light photon-absorption

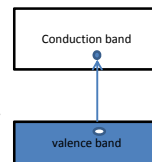
- In atoms, molecules, **isolated** in
- gas phase
  - solutions
  - within non-absorbing large molecules



$$E_{\text{photon}} = hf = \Delta \varepsilon_{\text{orbital}}$$

Only specific photon-energies are absorbed

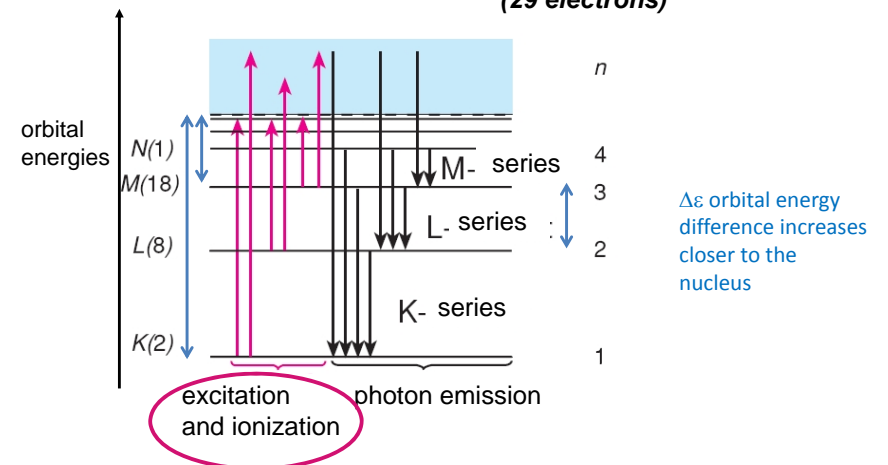
- In condensed phase (crystalline) materials



$$E_{\text{photon}} = hf \geq \Delta \varepsilon_{\text{gap}}$$

But metals! No gap! Broad range of photon-energies are absorbed

## Electronic orbital energies in an isolated **Cu** atom (29 electrons)



The electronic state is called **excited** if there is another arrangement of electrons in the electronic states when the total energy of them is lower.

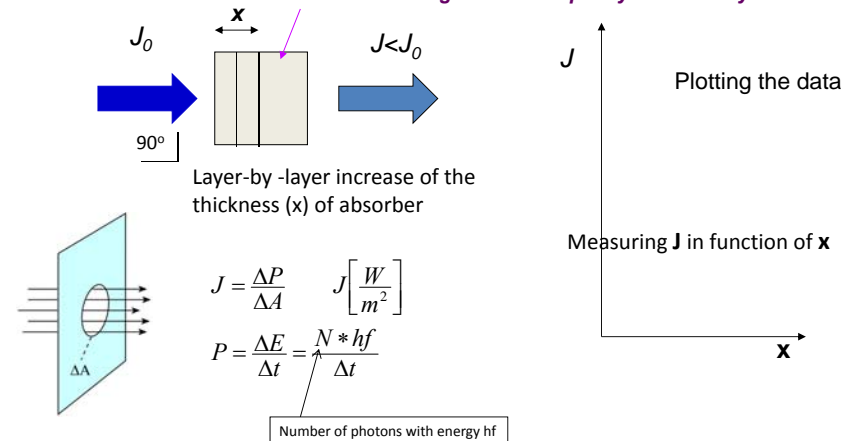
## Description of the phenomenon of light absorption

The general law of the attenuation of radiation intensity by absorption

Experiment: simple conditions:

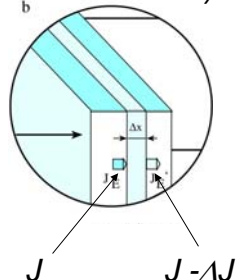
parallel beam at right angle to the surface

Absorber: homogeneous for quality and density



Outcome of the experiment:

For each elementary step in the process of absorption



$$\Delta J = -\mu \cdot \Delta x \cdot J$$

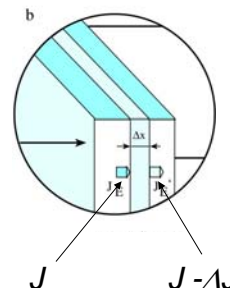
The decrease is proportional to the thickness of absorber  $\Delta x$  and  $J$  what is the intensity at the layer-element

stepwise application

$$J = J_0 \left[ \left( 1 - \frac{1}{n} \right)^n \right]^{\mu \Delta x} \quad \mu \Delta x = \frac{1}{n}$$

$$\left( 1 - \frac{1}{n} \right)^{-n} \xrightarrow{n \rightarrow \infty} e = 2.7182818 \dots$$

One elementary step in the process of absorption



$$\Delta J = -\mu \cdot \Delta x \cdot J$$

The decrease is proportional to the thickness of absorber  $\Delta x$  and  $J$  what is the intensity at the layer-element

Macroscopic function

$$J = J_0 \cdot e^{-\mu x}$$

Exponential law of radiation attenuation by absorption

$\mu$  : linear absorption coefficient



$\mu$ : linear absorption coefficient

Depends on the

**quality of radiation** (photonenergy ( $\lambda$ ) of radiation, or kinetic energy of particles)

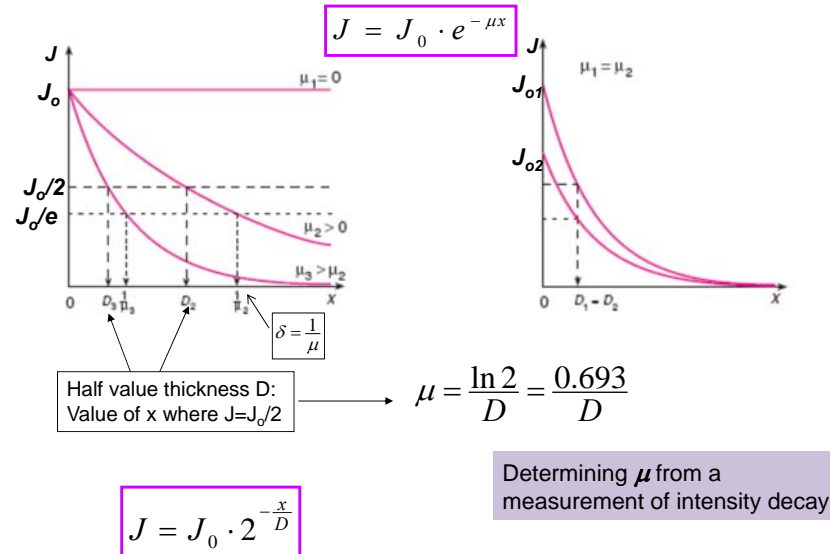
**quality of the absorbing material** (type of interaction)

**quantity of absorbing molecules** (density or concentration)

**Radiations that are attenuated according to the exponential law**

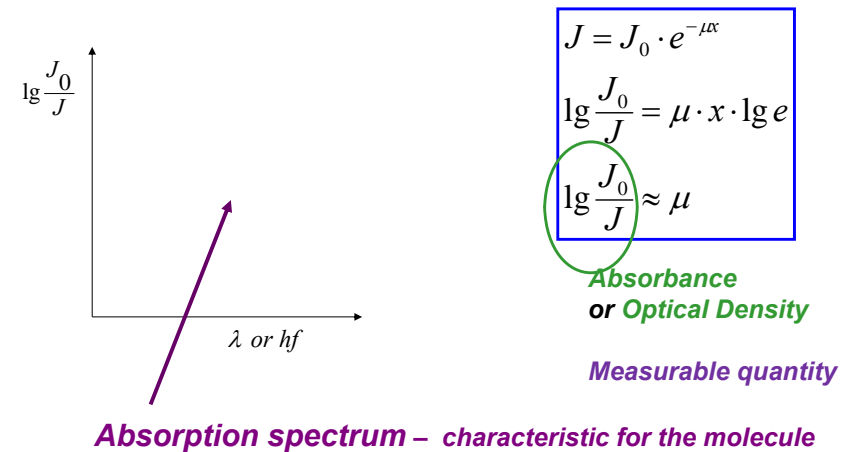
- Light (from UV through IR)
- X-ray
- $\gamma$ -radiation
- $\beta^-$  radiation up to  $x = 3-4$  times the half value thickness ( $D$ )

### Graphic representation of the absorption law

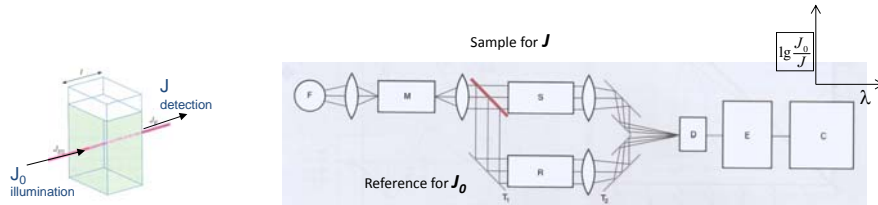


### Absorption spectroscopy - spectrophotometry

Measuring what photonenergies ( $\lambda$ -s) are absorbed - depends on  $\mu$



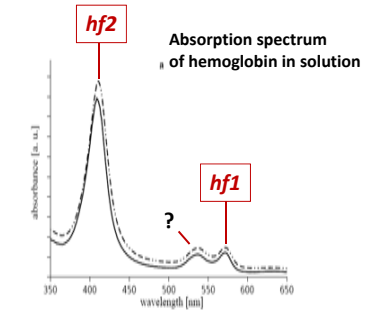
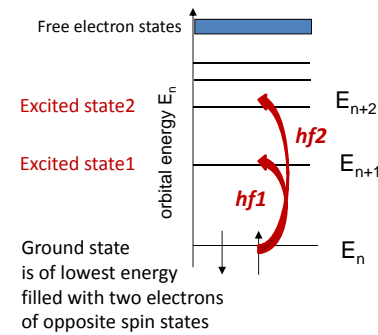
### Block diagram of an absorption spectrophotometer



Commercial absorption spectrophotometer is designed for measurements on **solutions** of absorbing molecules.

Sample e.g. in medical laboratory tests:  
solution in a glass cuvette of 1 cm thickness

### Schematics used to interpret the absorption spectrum by electronic transitions between atomic/molecular orbitals



**Simplified view:** - out of the filled orbitals, only that of the highest energy is shown:  $E_n$

- the highest occupied energy level is filled by two electrons of opposite spins  
(most of light absorbing/emitting molecules)

## Spectrophotometry

an application of absorption spectroscopy to determine the **concentration** of absorbing (color) molecules in **dilute solutions**

Basis: Beer-Lambert law

$$\mu(\lambda) = \varepsilon^*(\lambda) * c$$

$$J = J_0 e^{-\mu x}$$

$$\log \frac{J_0}{J} = \log e * \mu * x = \varepsilon(\lambda) * c * x$$

In dilute solutions, the absorbance (or optical density) at a fixed wavelength is directly proportional to the molar concentration ( $x=1$  cm)

Proportionality constant: **molar extinction** (coefficient)

measurable by spectrophotometer

measurable by a solution of known concentration

See lab manual for applications .....

Thank you for your attention!

