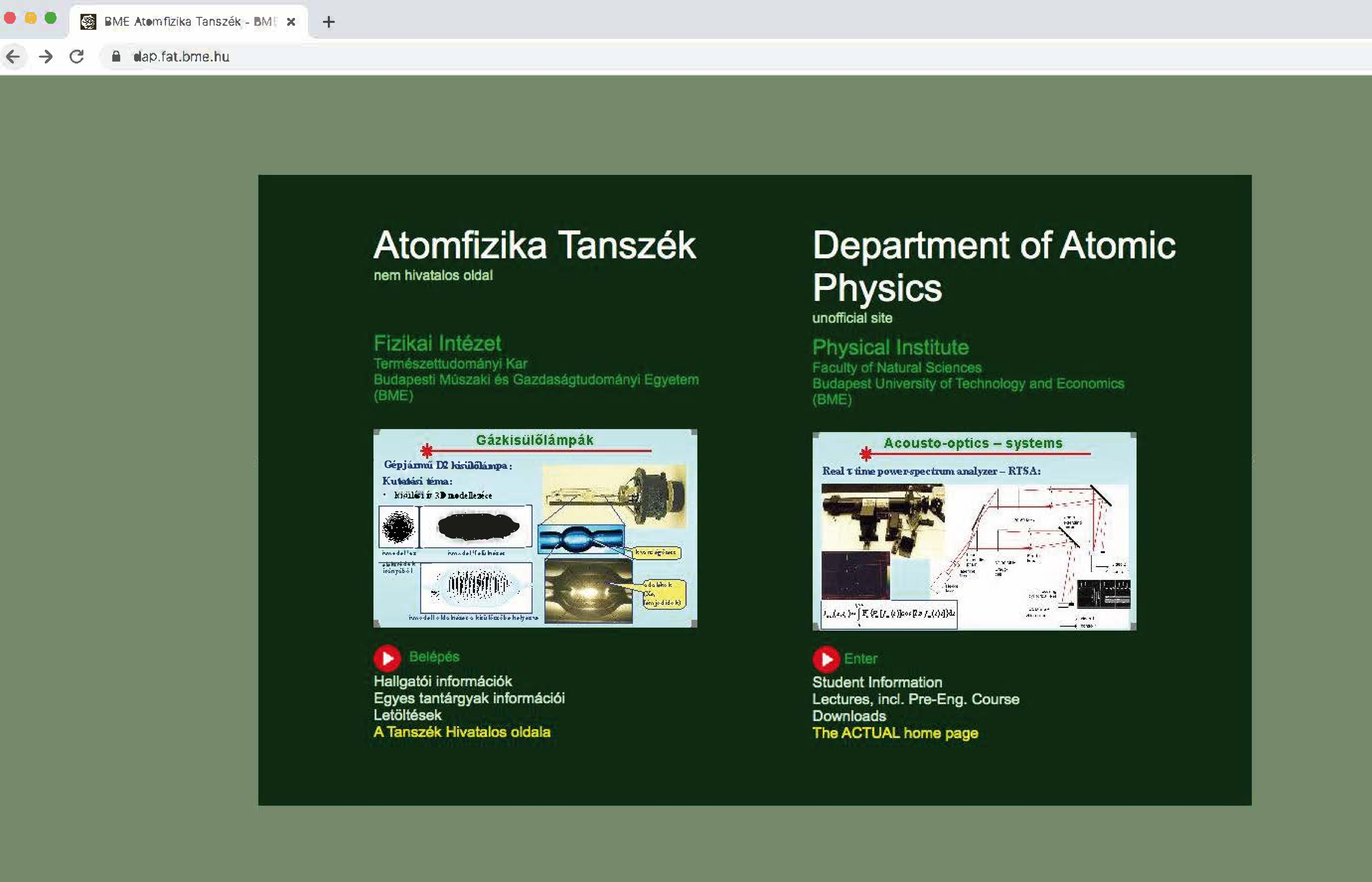
Peter Richter Andras Solyom

BMETE11MX33 - Fizika 3 (ENG) - H: 12:15-14:00 , Cs: 10:15-12:00

BMETE14MX00 - Modern fizika vegyészmérnököknek (ENG) H: 12:15-14:00 , Cs: 10:15-12:00



Atomfizika Tanszék

nem hivatalos oldal

Fizikai Intézet

Természettudományi Kar
Budapesti Műszaki és Gazdaságtudományi Egyetem
(BME)

Gázkisülőlámpák

Gépjármű D2 kisülőlámpa:

Kutatási téma:

- kisülési ív 3D modellezése

Belépés

Hallgatói információk
Egyes tantárgyak információi
Letöltések
A Tanszék Hivatalos oldala

Department of Atomic Physics

unofficial site

Physical Institute

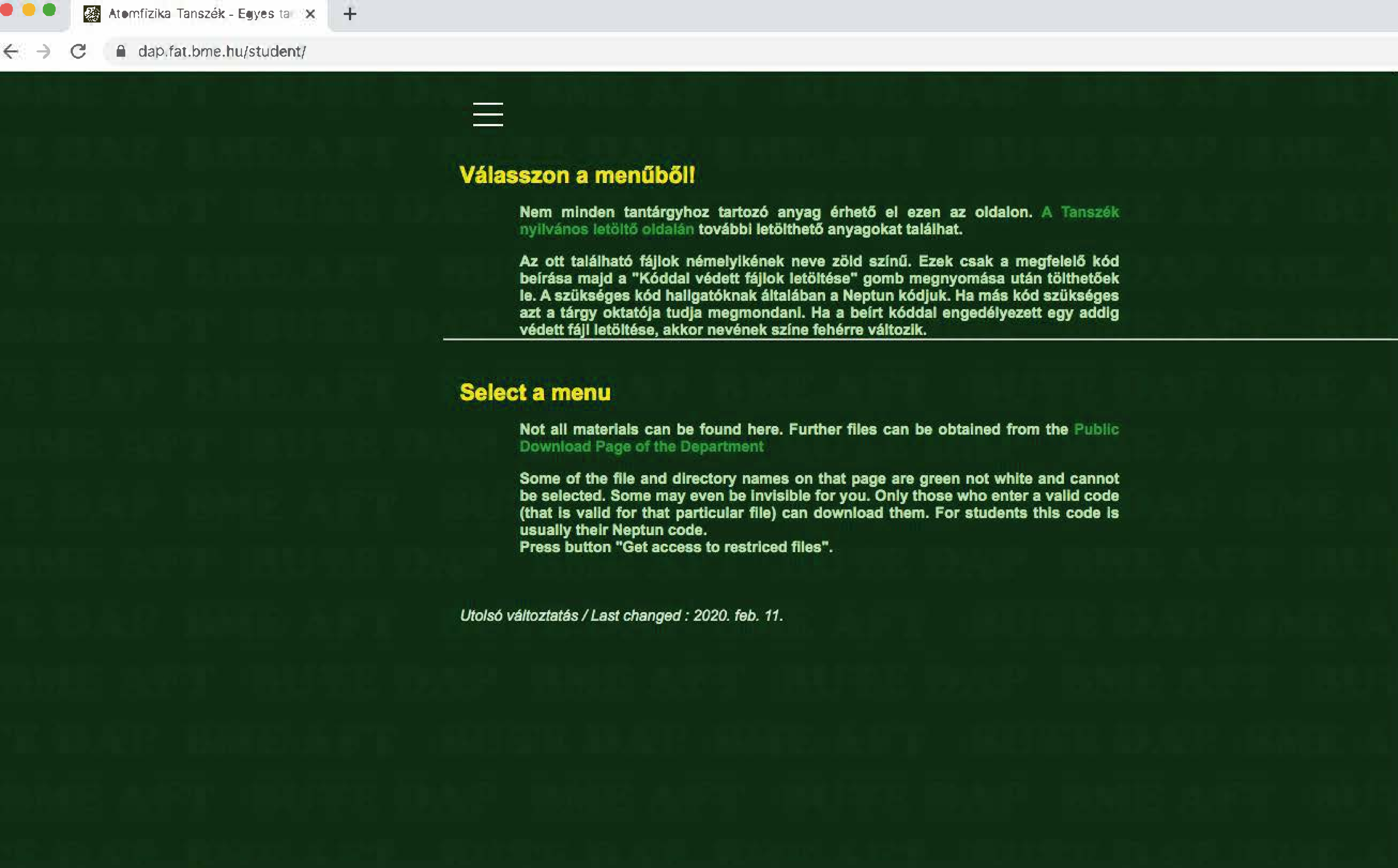
Faculty of Natural Sciences
Budapest University of Technology and Economics
(BME)

Acousto-optics – systems

Real τ time power-spectrum analyzer – RTSA:

Enter

Student Information
Lectures, incl. Pre-Eng. Course
Downloads
The ACTUAL home page



Válasszon a menűből!

Nem minden tantárgyhoz tartozó anyag érhető el ezen az oldalon. A Tanszék nyilvános letöltő oldalán további letölthető anyagokat találhat.

Az ott található fájlok némelyikének neve zöld színű. Ezek csak a megfelelő kód beírása majd a "Kóddal védett fájlok letöltése" gomb megnyomása után tölthetőek le. A szükséges kód hallgatóknak általában a Neptun kódjuk. Ha más kód szükséges azt a tárgy oktatója tudja megmondani. Ha a beírt kóddal engedélyezett egy addig védett fájl letöltése, akkor nevének színe fehérre változik.

Select a menu

Not all materials can be found here. Further files can be obtained from the Public Download Page of the Department

Some of the file and directory names on that page are green not white and cannot be selected. Some may even be invisible for you. Only those who enter a valid code (that is valid for that particular file) can download them. For students this code is usually their Neptun code.
Press button "Get access to restriced files".

Utolsó változtatás / Last changed : 2020. feb. 11.

A főoldalra

A Hallgatói Információkhoz

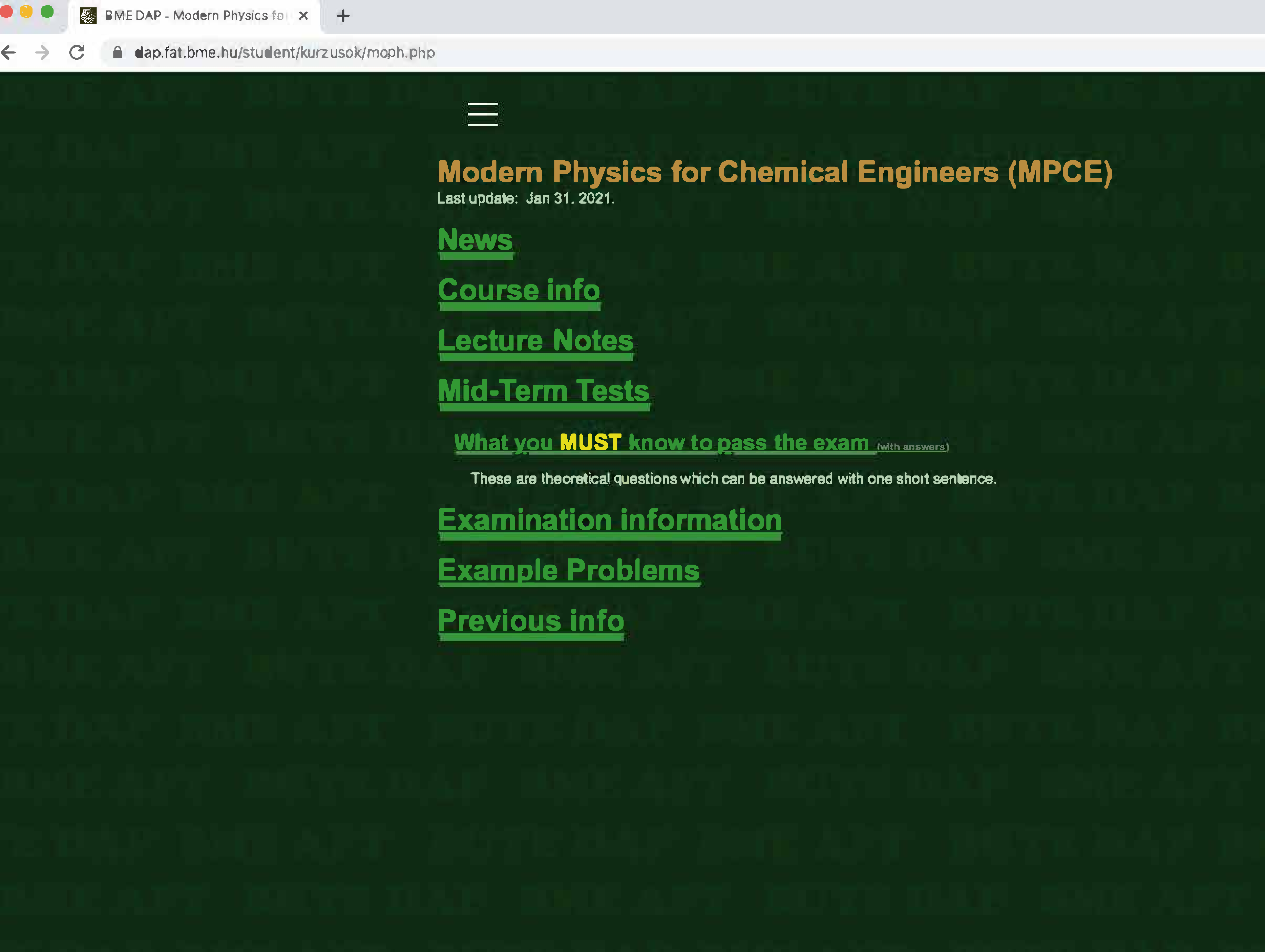
A Tanszéki fájl Szerverre

Lézerfizika / Laser Physics

Modern Physics for Chemical Engineers (MPCE)

Physics 3 (MSc)

Programozás 3 - 2020/2021 I. félév



Modern Physics for Chemical Engineers (MPCE)

Last update: Jan 31. 2021.

News

Course info

Lecture Notes

Mid-Term Tests

What you **MUST** know to pass the exam (with answers)

These are theoretical questions which can be answered with one short sentence.

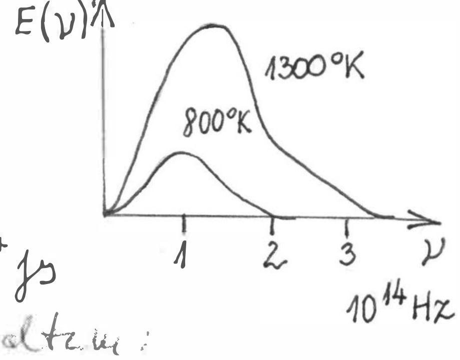
Examination information

Example Problems

Previous info

Quantum Mechanics   Introduction

Alonso-Finn
Fundamental University
Physics Vol. III.



- Black body radiation

$\frac{1}{V} E(\nu)\, d\nu$

Planck : material → oscillators
abs. & em. in $E = h\nu$ quanta

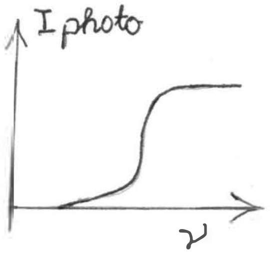
$$E(\nu) = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} \qquad h = 6{,}6 \cdot 10^{-34}\ Js$$

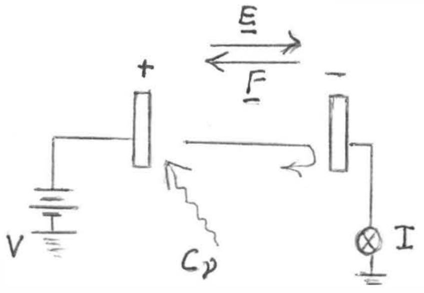
Wien : $\lambda_{max} \cdot T = \text{const.}$

Stefan - Boltzm. :

$$\int_0^\infty E(\nu)\, d\nu = \sigma T^4$$

- Photoelectric effect





$I = 0$ at $V = V_0$

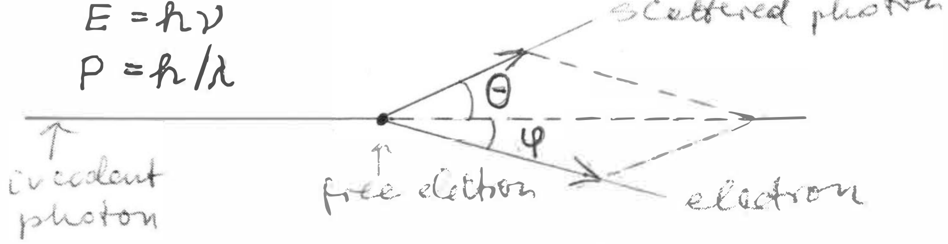
$eV_0 = E_{kin.max} = h\nu - \phi$

ϕ = work function

- Compton effect

$E = h\nu$
$p = h/\lambda$

$E' = h\nu'$
$p' = h/\lambda'$

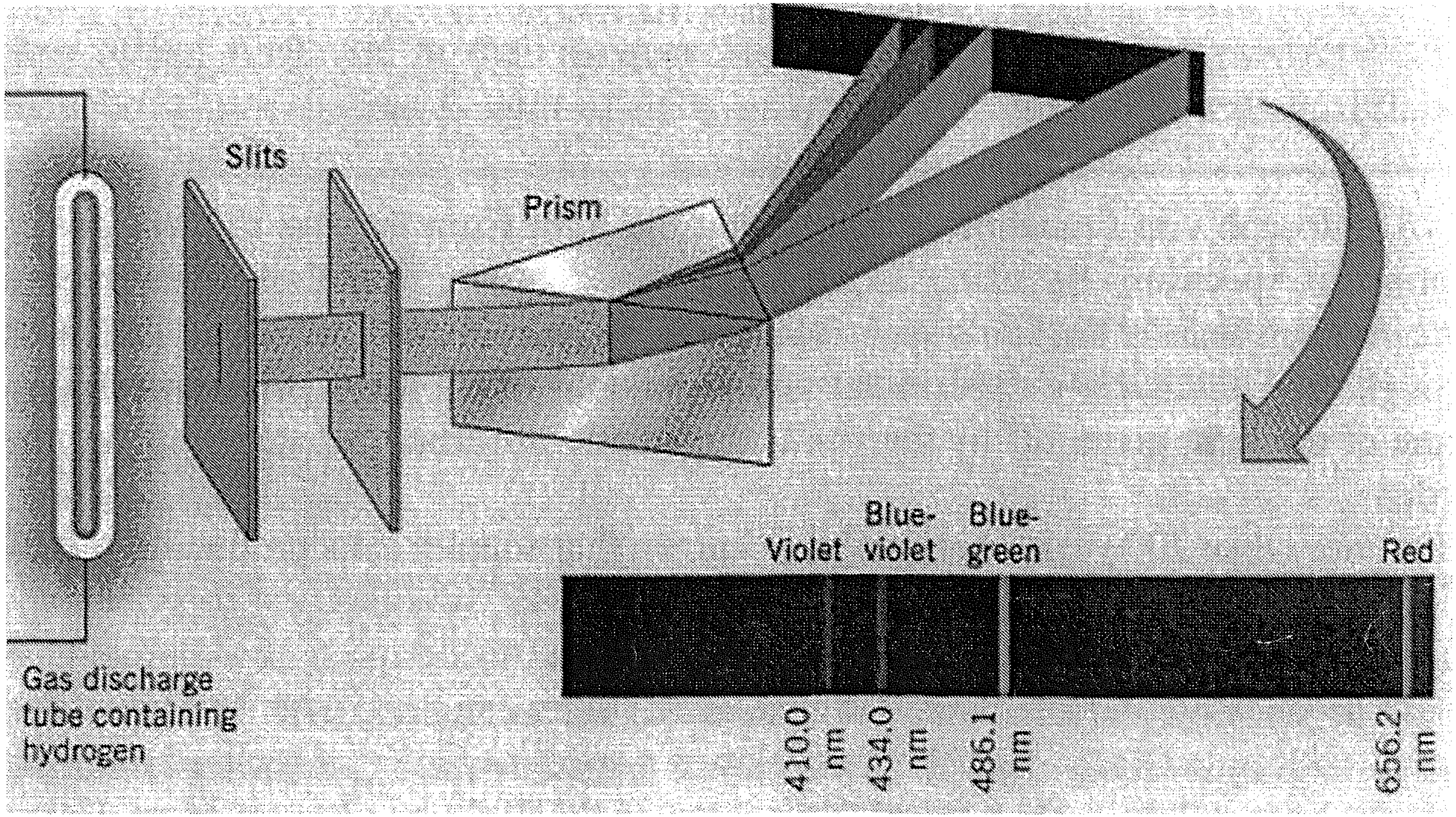


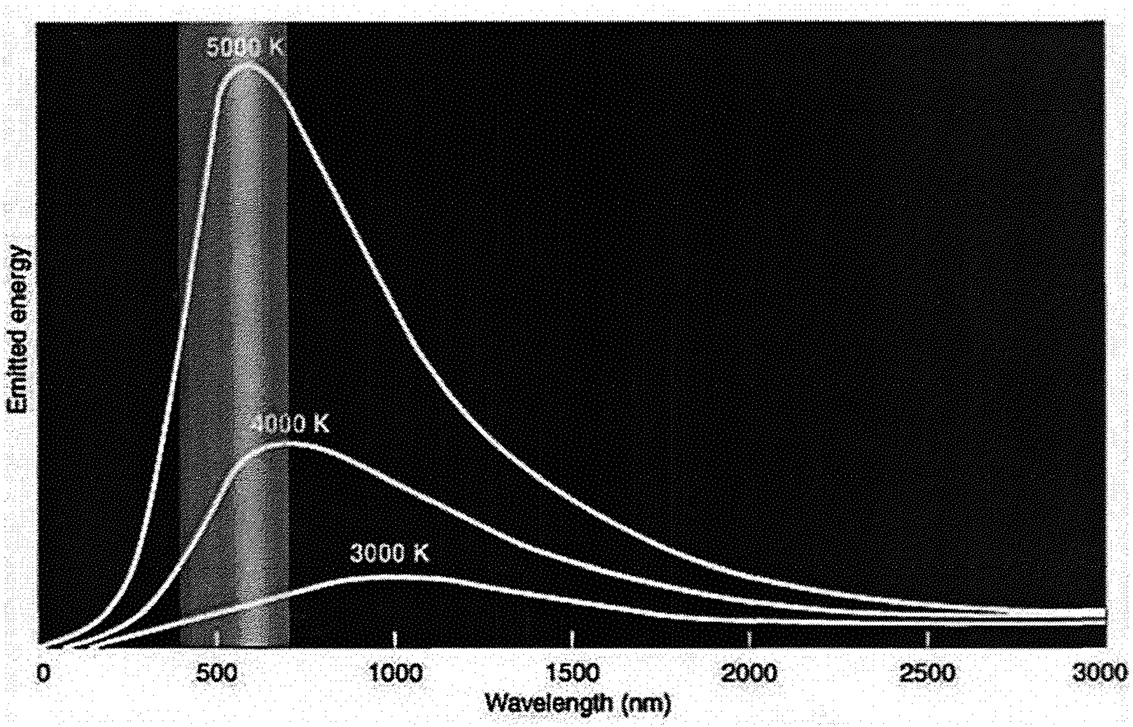
$$\lambda' - \lambda = \lambda_c (1 - \cos\Theta)$$

Calculating as collision / conservation of energy and momentum /

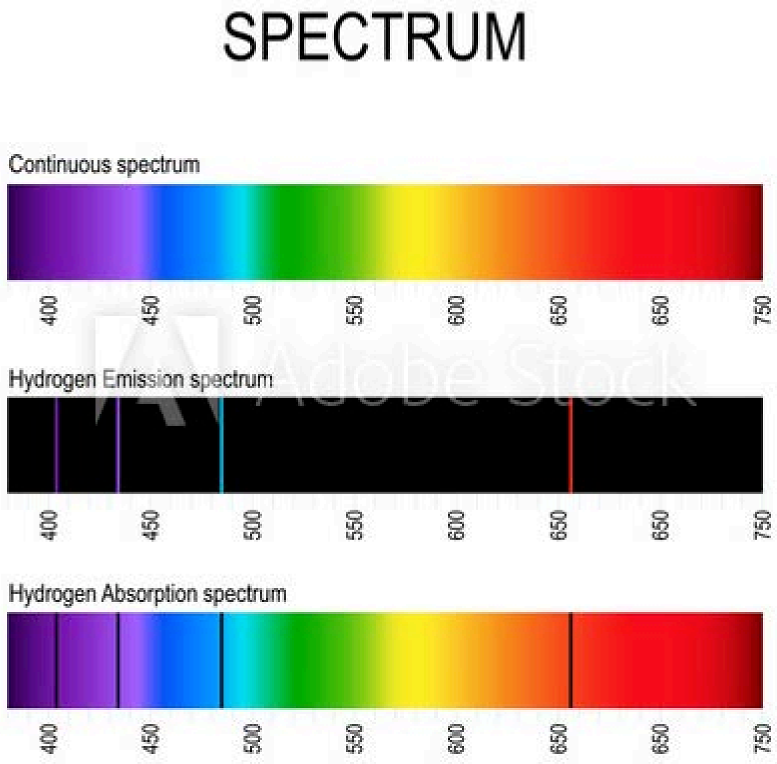
$$\lambda_C = \frac{h}{m_e \cdot c}$$

$$\left.\begin{array}{l} \text{Maxwell} : E = c \cdot p \\ \text{relativity} : E = c\sqrt{m_0^2 c^2 + p^2} \end{array}\right\} \rightarrow m_0 = 0$$


Slits
Prism
Gas discharge tube containing hydrogen
Violet
Blue-violet
Blue-green
Red
410.0 nm
434.0 nm
486.1 nm
656.2 nm



Spectrometer


SPECTRUM
Continuous spectrum
400
450
500
550
600
650
650
750
Hydrogen Emission spectrum
400
450
500
550
600
650
650
750
Hydrogen Absorption spectrum
400
450
500
550
600
650
650
750

$$\bar{E}_x = \bar{E}_{x_0} \sin\left(n_x \frac{\pi}{a} x\right) \sin\left(n_y \frac{\pi}{a} y\right) \sin\left(n_z \frac{\pi}{a} z\right)$$

$\bar{E}_y =$

$\bar{E}_z =$

$$\Delta \underline{\bar{E}} - \frac{1}{c^2} \frac{\partial^2 \bar{E}}{\partial t^2} = 0 \quad \rightsquigarrow$$

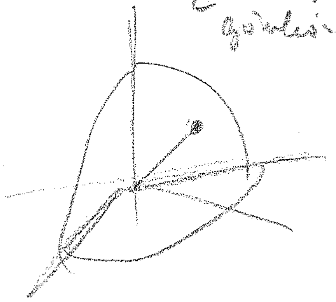
$$\frac{d^2 \bar{E}_x}{dt^2} + 4\pi^2 \nu_n^2 \bar{E}_x = 0$$

$$\nu_n = \frac{c}{2a} \sqrt{n_x^2 + n_y^2 + n_z^2}$$

$$\nu_n < \nu_{max} \longrightarrow n_x^2 + n_y^2 + n_z^2 \leq \frac{4a^2 \nu_{max}^2}{c^2}$$

$R = 2a \frac{\nu_{max}}{c}$ sugarú gömbcikkből!

$$\frac{1}{8}\left(\frac{4\pi}{3} R^3\right) = \frac{4\pi}{3} \frac{a^3 \nu_{max}^3}{c^3}$$



Polarizáció → ×2

$$Z = \frac{8\pi}{3} \frac{V \cdot \nu^3}{c^3}$$

Density of modes $\quad dZ(\nu) = \frac{8\pi V}{c^3} \nu^2 d\nu$

∀ mode → degree of freedom (harmonic osc.)

Thermal (stat) equilibr. → $k_B T$ energy = $\bar{E}$

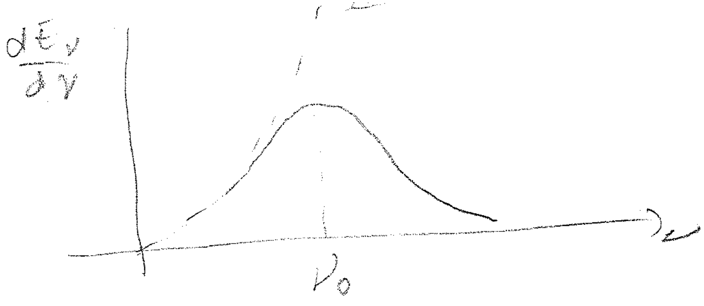
$$dE_\nu(T) = \bar{E}\, dZ(\nu) = k_B T \frac{8\pi V}{c^3} \nu^2 d\nu \longrightarrow \infty \text{ with } \nu!$$

UV catastrophy!

Total energy

$$E = \frac{8\pi V}{c^3} k T \int_0^\infty \nu^2 d\nu = \infty \quad !$$

Rayleigh-Jeans



Assumption: energy of a mode $\varepsilon_n = n \cdot \varepsilon_0 \quad n = 0, 1, 2 \dots$

Statistical equilibr.: number of modes with $\varepsilon_n \rightarrow N_n = N \cdot \frac{e^{-\frac{\varepsilon_n}{kT}}}{\sum_n e^{-\varepsilon_n/kT}}$
(Boltzmann)

Total energy: $E = \sum_{n=0}^{\infty} \varepsilon_n N_n = N \frac{\sum_n \varepsilon_n e^{-\frac{\varepsilon_n}{kT}}}{\sum_n e^{-\varepsilon_n/kT}}$

Average energy of one mode

$$\bar{\varepsilon} = \frac{E}{N} = \frac{\sum_n \varepsilon_n e^{-\frac{\varepsilon_n}{kT}}}{\sum_n e^{-\frac{\varepsilon_n}{kT}}} = \frac{\sum_n n \varepsilon_0 e^{-\frac{n \cdot \varepsilon_0}{kT}}}{\sum_n e^{-n \varepsilon_0/kT}}$$

Denominator: geometrical series $= \frac{1}{1 - e^{-\varepsilon_0/kT}}$

Numerator $\left(\xi = -\frac{1}{kT}\right)$: $\sum_n n \varepsilon_0 e^{\xi n \varepsilon_0} = \frac{d}{d\xi} \underbrace{\sum_n e^{\xi n \varepsilon_0}}_{\frac{1}{1 - e^{\xi \varepsilon_0}}} = \frac{\varepsilon_0 e^{\xi \varepsilon_0}}{(1 - e^{\xi \varepsilon_0})^2}$

$$\bar{\varepsilon} = \frac{\frac{\varepsilon_0 e^{-\frac{\varepsilon_0}{kT}}}{(1 - e^{-\frac{\varepsilon_0}{kT}})^2}}{\frac{1}{(1 - e^{-\varepsilon_0/kT})}} = \frac{\varepsilon_0}{e^{\varepsilon_0/kT} - 1} \quad \Bigg| \quad = \frac{\varepsilon_0}{\varepsilon_0/kT} = kT$$

$e^{\frac{\varepsilon_0}{kT}} - 1 = 1 + \frac{\varepsilon_0}{kT} + \dots - 1 = \frac{\varepsilon_0}{kT}$

$\rightsquigarrow \bar{\varepsilon} = kT$

If $\varepsilon_0 \rightarrow 0 \rightarrow$ Rayleigh Jeans:

If $\varepsilon_0 \neq 0 \quad \varepsilon_0 = h\nu \quad h = 6 \cdot 10^{-34}$ Jsec

Planck

$$\bar{\varepsilon} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

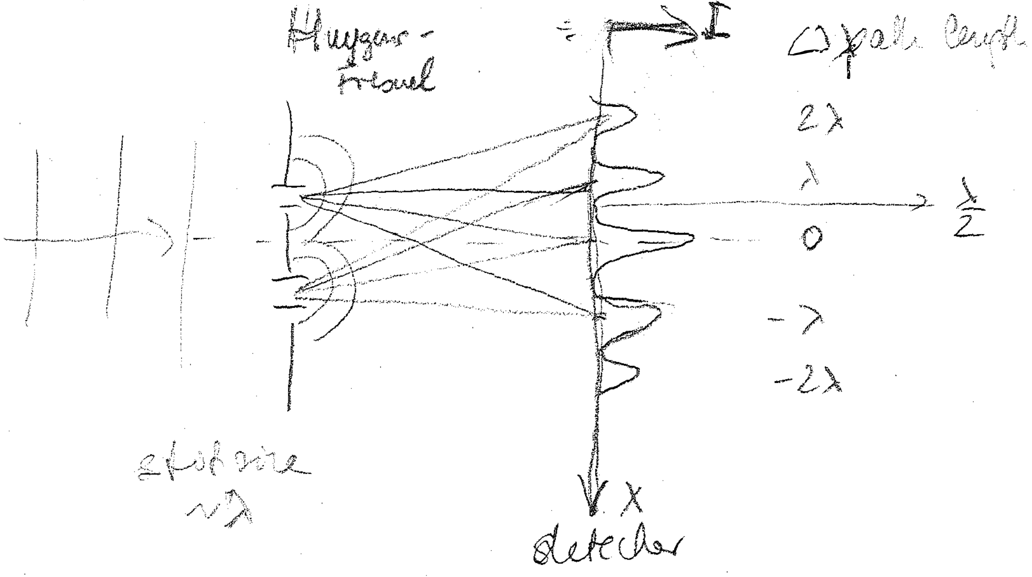
$$dE_\nu(T) = \bar{\varepsilon} \cdot Z(\nu) = \frac{8\pi V}{c^3} \frac{h\nu^3}{e^{h\nu/kT} - 1} d\nu$$

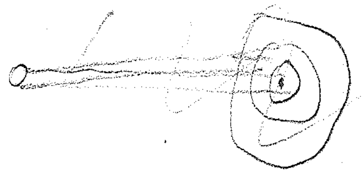
Planck's radiation law
h = Planck's constant

viene:
Fotoelektr. hatás
Compton eff

Wave → interference

Young's double slit interference

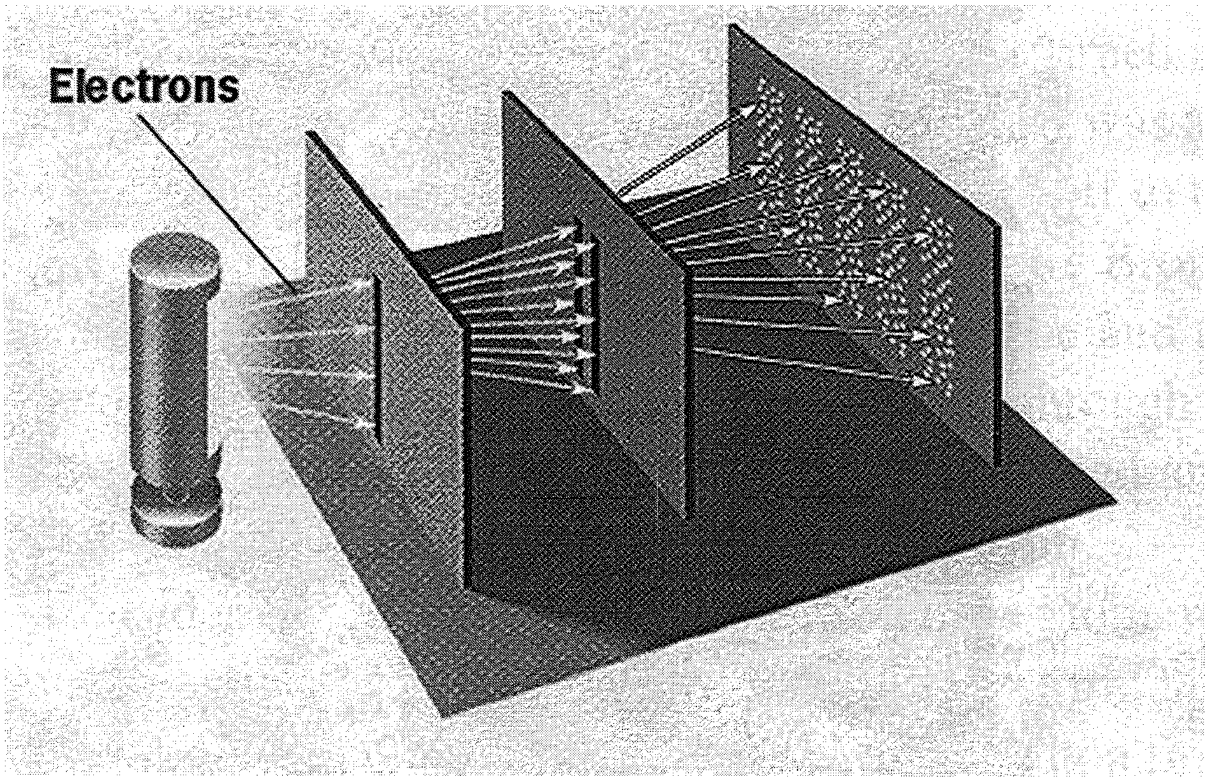


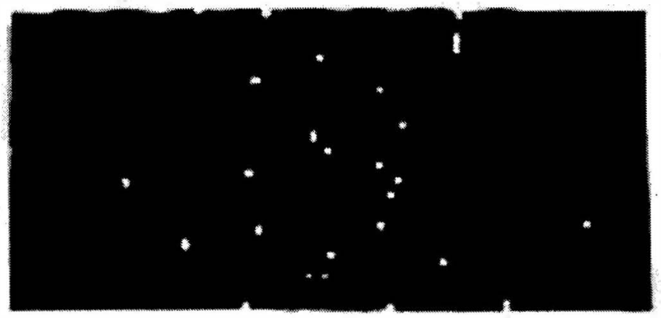


Wave packet $\Delta x \cdot \Delta k \sim 2\pi$ (Fourier tr)

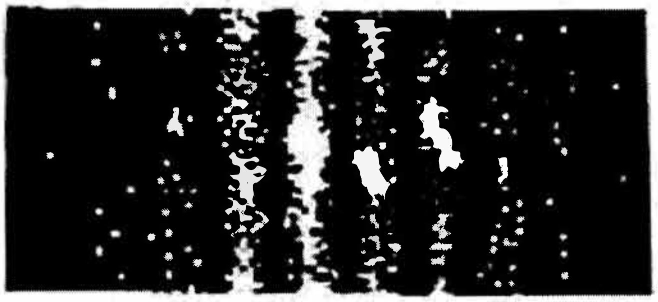
De Broglie $\lambda = \frac{h}{p} \rightsquigarrow k = \frac{2\pi}{\lambda} = \frac{2\pi}{h/p} = \frac{p}{\hbar}$ $(h = 6 \cdot 10^{-34}\,\mathrm{Js})$

$$\Delta x \cdot \Delta p \sim h$$

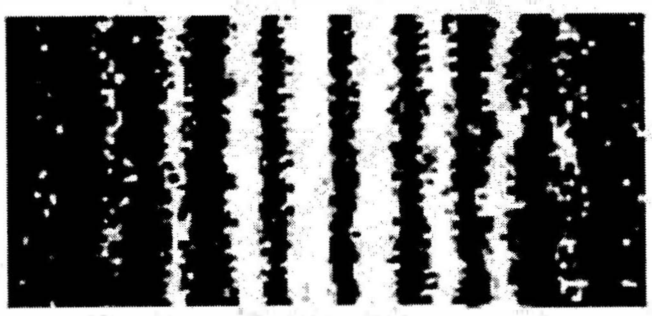

Electrons



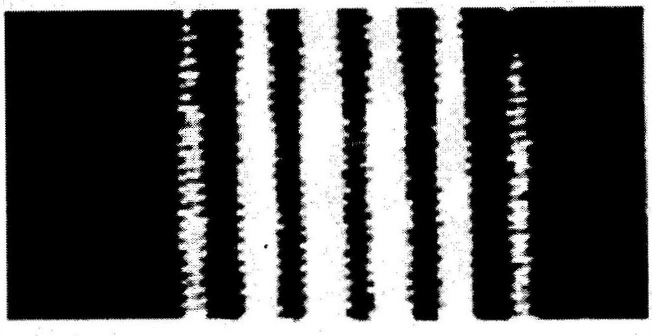
(a) After 28 electrons



(b) After 1000 electrons



(c) After 10,000 electrons

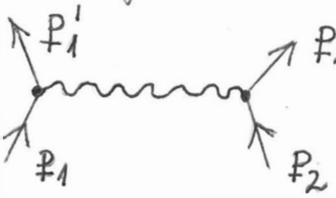


(d) Two slit electron pattern

- Photons

$E = h\nu$, $p = \frac{h}{\lambda}$ Description of interaction of electromagnetic waves with charged particles with a photon of energy E, momentum p

In general: electromagnetic interaction ≡ exchange of photons between charged particles



- Stationary states

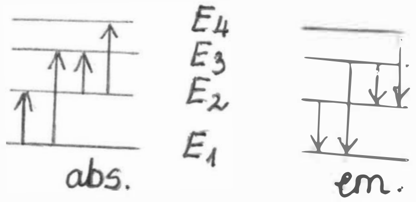
System of charged particles: atom, molecule, nucleus etc.

- resonance frequencies
- absorption spectrum
- ground state, excited states
- absorption frequencies = emission frequencies

Bohr: Transition between states with energies E and E' $h\nu = E' - E$

Disrect energy levels → stationary states

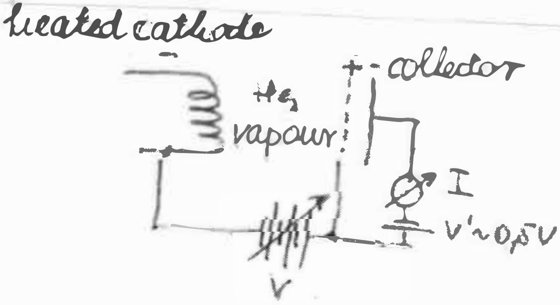
$A + h\nu \longrightarrow A^*$ abs.
$A^* \longrightarrow A + h\nu$ em.

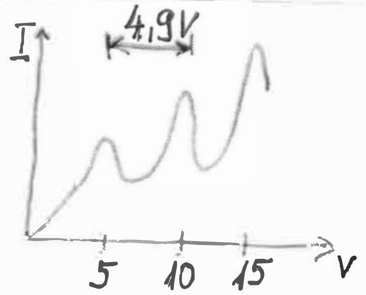


- Contradiction with classical mechanics

quantization of energy
electron circulates but does not radiate

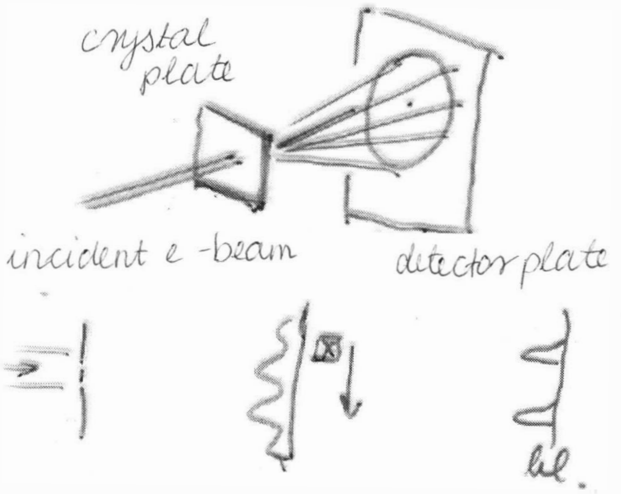
Franck-Hertz experiment

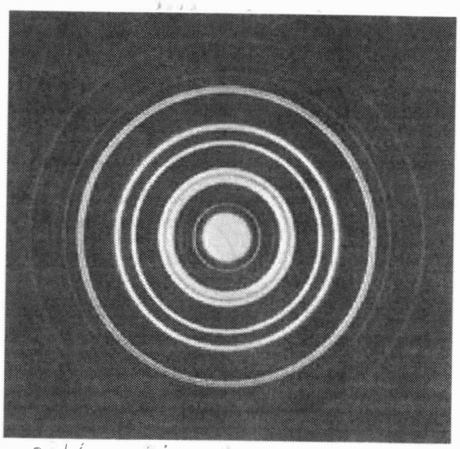




- Wave particle duality

Electrons may behave like waves: interference, diffr.





Diffraction image (powder sample)

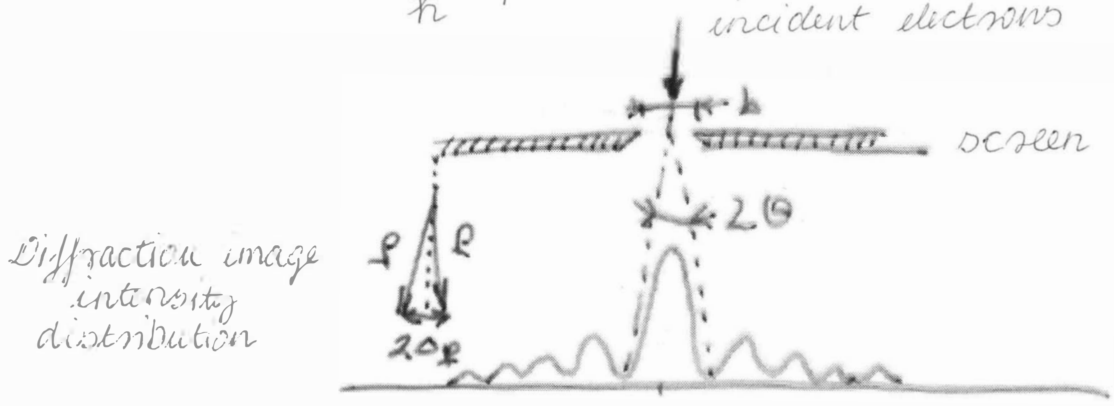
$\lambda = \frac{h}{p}$ de-Broglie wavelength

Free particle → wave packet

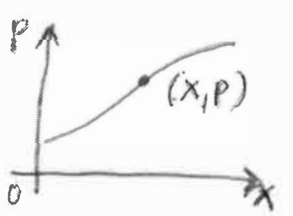
- Heisenberg uncertainty relationship

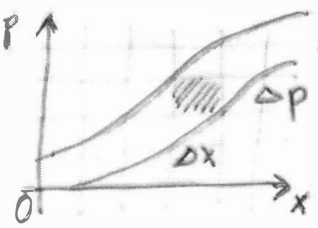
Wave packet → Fourier transform $\Delta x \cdot \Delta k \approx 2\pi$

$\Delta k = \frac{1}{\hbar} \Delta p \rightsquigarrow \Delta x \Delta p \sim h$



Motion in phase space:





Energy - time

$\Delta t \cdot \Delta E \sim h$ / Fourier tr. of wave packet

$\Delta t \; \Delta \omega \sim 2\pi \qquad \Delta \omega = \frac{\Delta E}{\hbar}$

Stationary state → lifetime → linewidth

Határozatlansági reláció

$$\Delta x \, \Delta p \geq h = 6{,}6 \cdot 10^{-34} \, Js$$

Makrovilág

pl $\Delta x = 1 \mu m = 10^{-6} m$

$$\Delta p \geq \frac{6{,}6 \cdot 10^{-34} \, kg \frac{m^2}{s}}{10^{-6} m} = 6{,}6 \cdot 10^{-28} \, kg \frac{m}{s}$$

pl $\varrho = 10^3 \frac{kg}{m^3}$ $1 \mu m^3 = 10^{-18} m^3 \rightarrow m = 10^{-15} kg$

$$\Delta v = \frac{\Delta p}{m} = \frac{6{,}6 \cdot 10^{-28} \, kg \frac{m}{s}}{10^{-15} kg} = 6{,}6 \cdot 10^{-13} \frac{m}{s} \approx 0$$

Mikrovilág

atom $\Delta x \approx 0{,}1 nm = 10^{-10} m$

$$\Delta p \geq \frac{6{,}6 \cdot 10^{-34} \, kg \frac{m^2}{s}}{10^{-10} m} = 6{,}6 \cdot 10^{-24} \, kg \frac{m}{s}$$

elektron $m_{el} = 10^{-30} kg$

$$\Delta v = \frac{\Delta p}{m} \geq 6{,}6 \cdot 10^{6} \frac{m}{s} \quad ! \quad 0{,}02 \cdot c$$

H atom $m_p = 1850 \cdot m_{el} = 18 \cdot 10^{-28} kg$

$$\frac{1}{2} m v^2 = \frac{3}{2} kT \qquad v = \sqrt{\frac{3kT}{m_{atom}}} = \sqrt{\frac{3 \cdot 1{,}38 \cdot 10^{-23} \frac{J}{K} \cdot 200 K}{18 \cdot 10^{-28} kg}} =$$

$$= \sqrt{\frac{80\cancel{0} \cdot 10^{-24}}{18 \cdot 10^{-28}}} \approx 2 \cdot 10^{2} \frac{m}{s} = 200 \frac{m}{s}$$

Wave - particle duality

Black body
Photoelectric effect
Compton [illegible]
interference

wave : ν, λ $\quad \left(\omega = 2\pi\nu \quad k = \frac{2\pi}{\lambda} \right)$

particle : E, p

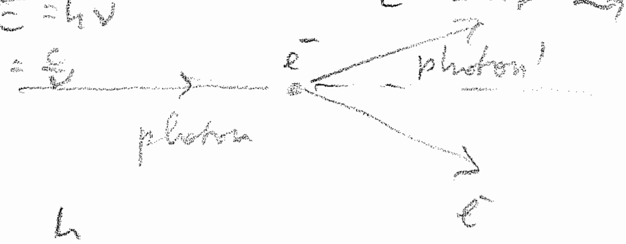
De - Broglie $\quad \lambda = \frac{h}{p} \quad \nu = \frac{E}{h} \quad \rightsquigarrow$

$$p = \frac{h}{\lambda} = \frac{h}{2\pi/k} = \hbar \cdot k \qquad E = \hbar\omega \qquad \hbar = \frac{h}{2\pi} \simeq 10^{-34}\,\mathrm{J\,sec}$$

Compton effect light scattering on free electron

$E = h\nu$

$\lambda = \frac{c}{\nu}$



$E' = h\nu' \rightsquigarrow \lambda' = \frac{c}{\nu'}$

$p' = \frac{h}{\lambda'}$

collision ;
conservation of
E, p

$p = \frac{h}{\lambda}$

" collision "

Electron diffraction

Quantum mechanics /2

Wave function, probability density, Schrödinger equation ④

- Motion of particles

Classical orbit ↓

Localized particle - standing wave - wavefunction $\psi(x)$

Wave intensity $\sim |\psi|^2$

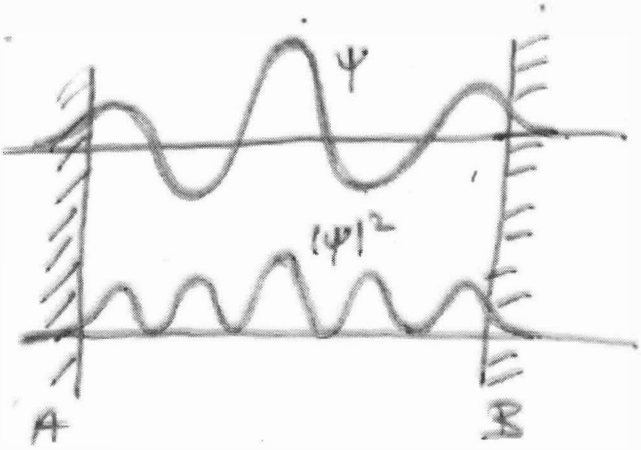
ψ complex ψ^* compl. conjugate $|\psi|^2 = \psi^*\psi$

Probability of finding the particle in a range Δx around $x = |\psi(x)|^2 dx$

In three dimension, Volume

$$P_V = \int_V |\psi(x,y,z)|^2 \, dx\,dy\,dz$$

$$\int_{\text{whole space}} |\psi|^2 \, dx\,dy\,dz = 1$$



particle moves between A and B

E.g.: Probability distribu of electron positi in an atom

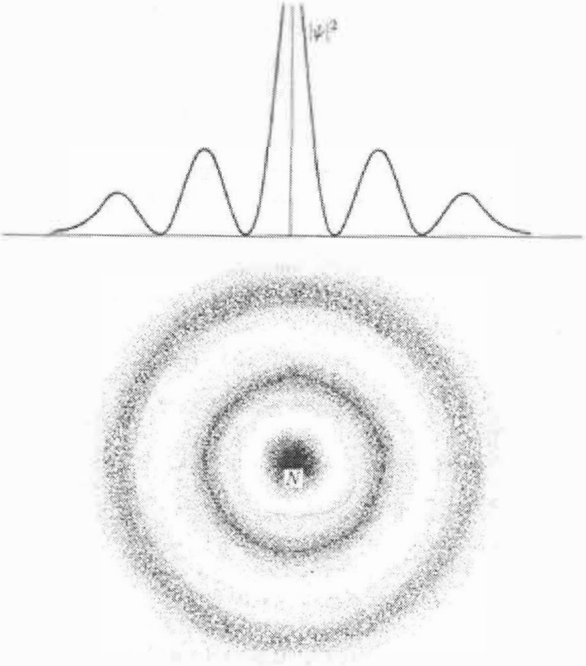


Fig. 2–2. Probability distribution for an electron in an atom.

- Question: how to determine ψ?

Depends on the forces acting on the particle as well ~~as~~ on the energy of the particle

Full energy: $E = \frac{p^2}{2m} + E_p \Leftarrow$ forces

Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + E_p(x)\psi = E\psi$$ (1dim., m=particle mass)

Intuitive derivation:

1 dim. wave equation: $\frac{d^2\xi}{dx^2} + k^2\xi = 0$ (in general)

$k = \frac{2\pi}{\lambda}$ wave number $p = \hbar k$ in quantum mech.

writing this to the wave equation:

$$\frac{d^2\psi}{dx^2} + \frac{p^2}{\hbar^2}\psi = 0$$

but from the full energy $E \rightsquigarrow p^2 = 2m[E - E_p]$

with this $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - E_p(x)]\psi = 0$

- Solutions

E.g. $\psi(x) = e^{ikx} \to |\psi|^2 = 1$: since $\Delta p = 0 \rightsquigarrow \Delta x \to \infty$

Principle of superposition ↑: ψ_1 and ψ_2 solution $\rightsquigarrow$

$\psi = a\psi_1 + b\psi_2$ — " —

$p = \hbar k$, $E = \frac{\hbar^2 k^2}{2m}$ particle moving +x dir. e^{ikx}

— " — — " — −x dir. e^{-ikx}

$\psi_1 = a \cdot e^{ikx}$ $\psi_2 = a e^{ik(x+b)}$

$\psi = \psi_1 + \psi_2$

$|\psi|^2 = 2a^2(1+\cos kb)$ — interference

Concrete solutions → boundary conditions ($E_p(x)$)

Quantum mechanics /3.

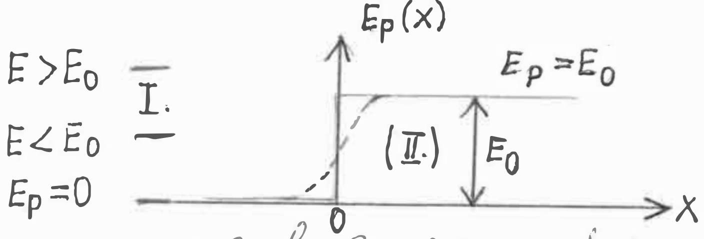
Potential step, potential box, harmonic oscillator, tunneling effect

— Potential step

$E_p(x) \rightarrow$

$E_p(x) = 0; \quad x < 0$

$E_p(x) = E_0; \quad x > 0$



- - - real case, e.g. free electrons in a metal near the surface

From the Schrödinger eq.: $\psi(x)$

a, $\underline{E < E_0}$

kinetic energy $E_k = E - E_0 < 0$ would be, when $x > 0$

$\rightsquigarrow$ particle cannot enter $x > 0$

$\underset{\sim}{\text{I.}}$: $\underset{\sim}{x<0}$ $\quad E_p = 0 \quad$ Schr.: $\dfrac{d^2\psi_1}{dx^2} + \dfrac{2mE}{\hbar^2}\psi_1 = 0$

$\psi_1 = Ae^{ikx} + Be^{-ikx}$ $\quad$ ($e^{-ikx} \rightarrow$ reflected particle)

II.: $\underset{\sim}{x>0}$ $\quad E_p = E_0 \quad$ Schr.: $\dfrac{d^2\psi_2}{dx^2} + \dfrac{2m(E-E_0)}{\hbar^2}\psi_2 = 0$

Introduce $\alpha^2 = \dfrac{2m(E_0 - E)}{\hbar^2}$

Schr. $\dfrac{d^2\psi_2}{dx^2} - \alpha^2\psi_2 = 0$

Solution: $e^{\mp\alpha x}$ $\quad$ but $e^{+\alpha x}$ would give particle in region II.

$\psi_2(x) = C'e^{-\alpha x}$

Surprising: $\psi_2(x) \neq 0 \rightarrow$ particle enters even if $E < E_0 \rightarrow$ no sharp boundary

Penetration is not very deep (fast decay)

Factors A, B, C from the continuity of ψ at $x = 0$

$\psi_1 = \psi_2$ and $\frac{d\psi_1}{dx} = \frac{d\psi_2}{dx}$ at $x=0$ $\rightsquigarrow$

$A + B = C$ and $ik(A-B) = -\alpha C$ from this

$\psi_1(x) = A\left(e^{ikx} + \frac{ik+\alpha}{ik-\alpha} e^{-ikx}\right)$, $\psi_2(x) = \frac{2ik}{ik-\alpha} A e^{-\alpha x}$

Incident intensity: $|\psi_{in}|^2 = |A|^2$

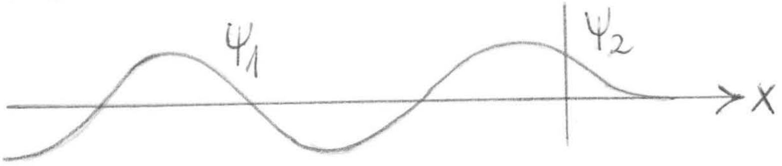
Reflected intensity: $|\psi_{refl.}|^2 = |B|^2 = \left|\frac{ik+\alpha}{ik-\alpha} A\right|^2 = |A|^2$

$\rightsquigarrow$ All particles are reflected even those that slightly penetrate region II.

$\psi_1(x)$ can be rewritten

$= \frac{2ik}{ik-\alpha} A\left(\cos kx - \frac{\alpha}{k}\sin kx\right)$

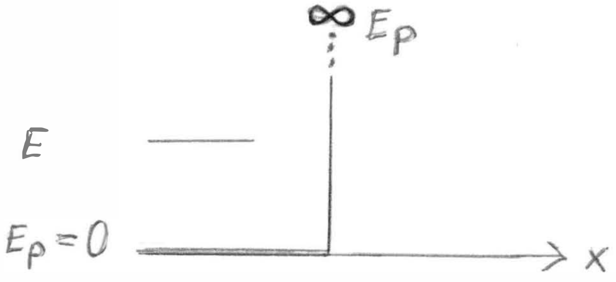
Spatial distribution of the real part of ψ_1 and ψ_2

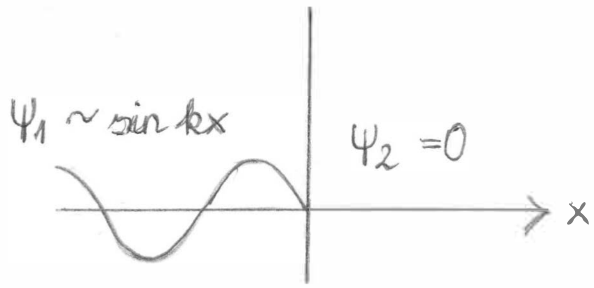


When the height of the step increases (E_0 increases)

$\rightsquigarrow$ α increases ψ_2 decays faster

$E_0 - \infty$





b. $E > E_0$ ⑧

classically : the particle moves through, only slightly slows down at $x = 0$

Region I: $\psi_1 = Ae^{ikx} + Be^{-ikx}$ solution

Region II: $k'^2 = \frac{2m(E-E_0)}{\hbar^2}$ with this

$$\frac{d^2\psi_2}{dx^2} + k'^2 \psi_2 = 0$$

Since all the particles move on

$$\psi_2(x) = C'e^{ik'x}$$

$A + B = C$ and $k(A-B) = k'C$ from the boundary conditions

Interesting: $B \neq 0 \rightarrow$ Reflection $\neq 0$

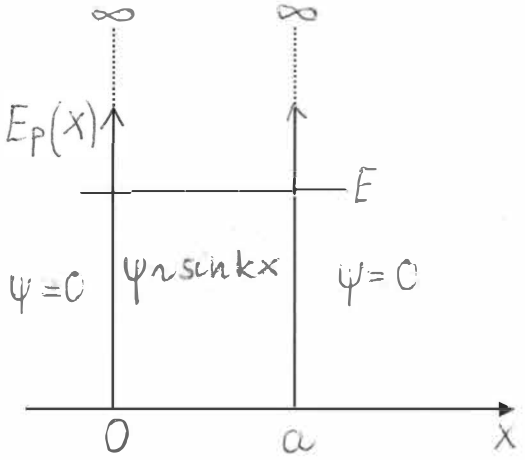
Potential box

E.g.: free particle in a container, electron in metal (ignore interaction with ions)

$E_\psi(x) = 0 \quad 0<x<a$

$\quad = \infty$ outside

$\rightsquigarrow \psi(x) = 0$ ~~out~~side



Inside:
Schr. e.:

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

$$k^2 = \frac{2mE}{\hbar^2}$$

$$\psi(X) = Ae^{ikx} + Be^{-ikx}$$

Boundary conditions: $\psi(x) = 0 \quad x = 0$ and $x = a$

$\longrightarrow \psi(0) = A + B = 0 \rightsquigarrow A = -B \rightsquigarrow$

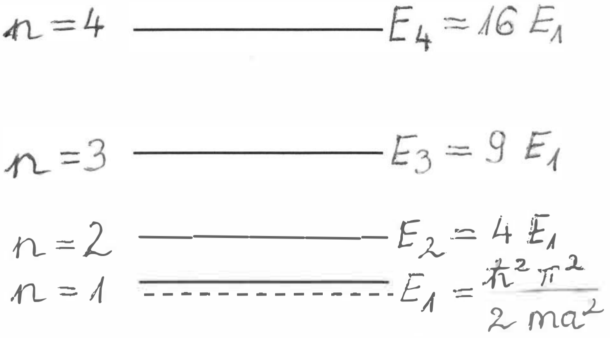
$\psi(X) = \left(Ae^{ikx} - e^{-ikx}\right) = 2iA \sin kx = C' \sin kx \quad C = 2iA$

$\longrightarrow \psi(a) = C' \sin ka = 0 \rightsquigarrow \sin ka = 0 \rightsquigarrow$

$k = n\frac{\pi}{a}$ <u>n = integer!</u> $p = \hbar\frac{n\pi}{a}$ momentum

The energy:

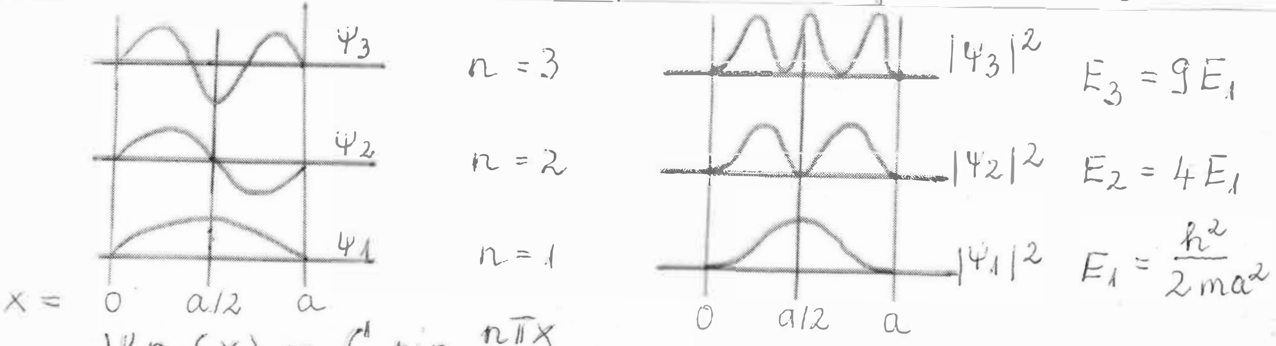
$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad E_n \sim n^2$$



Discreet energy values

This is ↑ when motion of the particle is limited in space.

The wavefunctions and the probability densities



$$\psi_n(x) = C' \sin\frac{n\pi x}{a}$$

The particle can exist only with energy larger then a minimal energy

If $n = 0 \rightsquigarrow k = 0 \rightsquigarrow \psi(x) \equiv 0 \rightsquigarrow |\psi|^2 = 0 \to$ no particle

$n = 1 \quad E_1 = \frac{\hbar^2 \pi^2}{2ma^2} = E_{min}$

This is the so called <u>0-point energy</u>

It follows from Heisenberg's uncertainty principle

$\Delta x \, \Delta p \geq h$ now: $\Delta x \sim a$ $\Delta p \sim 2p$ (moving back & forth)

$$a \cdot 2p \geq h \to p \geq \frac{\pi\hbar}{a} \to E = \frac{p^2}{2m} \geq \frac{\pi^2\hbar^2}{a^2}\frac{1}{2m} = E_{min} = E_1$$

$C \to$ from normalization

$$\int_{-\infty}^{\infty} |\psi_n|^2 dx = \int_0^a |\psi_n|^2 dx = C'^2 \underbrace{\int_0^a \sin^2\frac{n\pi x}{a} dx}_{1/2\, a} = 1 \rightsquigarrow C' = \sqrt{\frac{2}{a}}$$

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}$$

The wavefunctions are <u>orthogonal</u> i.e

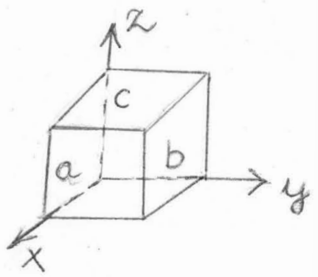
$$\int_{-\infty}^{\infty} \psi_n^* \psi_{n'} \, dx = 0 \quad \text{if} \quad n \neq n'$$

since

$$\int_0^a \sin\frac{n\pi x}{a} \sin\frac{n'\pi x}{a} dx = \frac{1}{2}\int_0^a \left[\cos\frac{(n-n')\pi x}{a} - \cos\frac{(n+n')\pi x}{a}\right] dx = 0$$

– Three dimensional / spatial / potential box

$$p_x = \frac{\pi \hbar n_1}{a} ; \quad p_y = \frac{\pi \hbar n_2}{b} ; \quad p_z = \frac{\pi \hbar n_3}{c}$$



$$E = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) =$$

$$= \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)$$

$$\Psi = C'' \sin \frac{n_1 \pi x}{a} \sin \frac{n_2 \pi y}{b} \sin \frac{n_3 \pi z}{c}$$

Cube box: $E = \frac{\pi^2 \hbar^2}{2ma^2}\left(n_1^2 + n_2^2 + n_3^2\right) = \frac{\pi^2 \hbar^2}{2ma^2} \varkappa^2 = E_1 \varkappa^2$

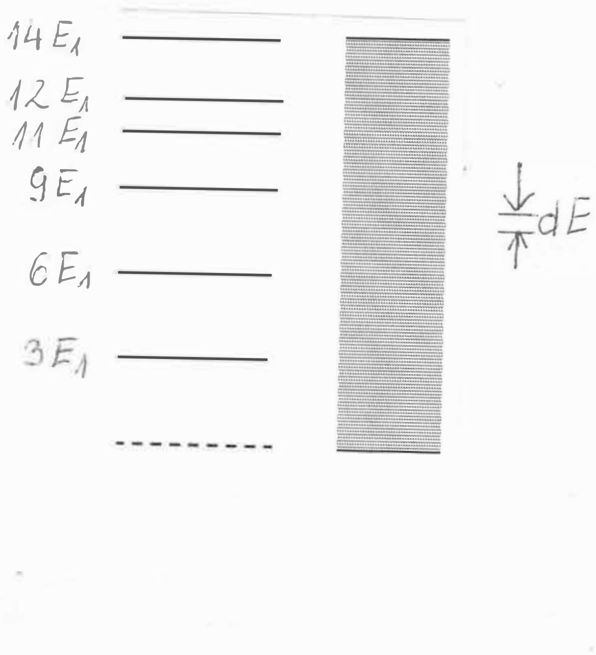
$$\varkappa^2 = n_1^2 + n_2^2 + n_3^2$$

The same $\varkappa$ with different n_1, n_2, n_3 → degenercy

Possible energy	n_1, n_2, n_3 combination	degree of degeneracy (g)
$3\ E_1$	$(1,1,1)$	1
$6\ E_1$	$(2,1,1)\ (1,2,1)\ (1,1,2)$	3
$9\ E_1$	$(2,2,1)\ (2,1,2)\ (1,2,2)$	3
$11\ E_1$	$(3,1,1)\ (1,3,1)\ (1,1,3)$	3
$12\ E_1$	$(2,2,2)$	1
$14\ E_1$	$(1,2,3)\ (3,2,1)\ (2,3,1)$ $(1,3,2)\ (2,1,3)\ (3,1,2)$	6

Big box

a is large → gap between energy levels is small
dense energy states



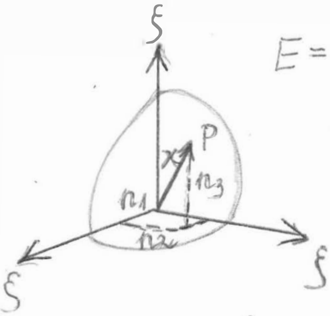
Number of states between energies $0 - E \equiv N(E)$

Volume of $\frac{1}{8}$-th of sphere with radius κ

$$N(E) = \frac{1}{8}\,\frac{4\pi\kappa^3}{3} = \frac{1}{8}\,\frac{4\pi}{3}\left(\frac{E}{E_1}\right)^{3/2} =$$

$$= \frac{\pi}{6}\,a^3\left(\frac{2mE}{\pi^2\hbar^2}\right)^{3/2} =$$

$$= \frac{8\pi V}{3h^3}\,(2m^3)^{1/2}\,E^{3/2}$$



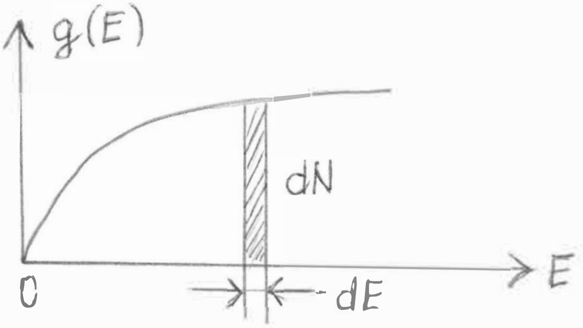
$$E = E_1\kappa^2$$

$$\kappa = \sqrt{\frac{2mE}{\pi^2\hbar^2}}\cdot a$$

$$V = a^3$$

Density of states:

$$g(E) = \frac{dN(E)}{dE} = \frac{4\pi V(2m^3)^{1/2}}{h^3}\,E^{1/2}$$



Harmonic oscillator

E.g. vibration of atoms in molecules or solids

$$E_p = \frac{1}{2} k x^2$$

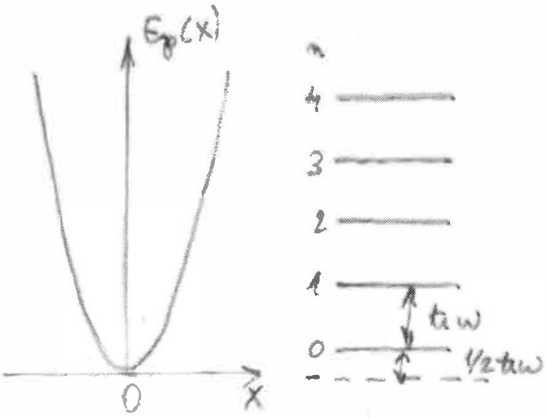
Schr. eq.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2} k x^2 \psi = E\psi$$

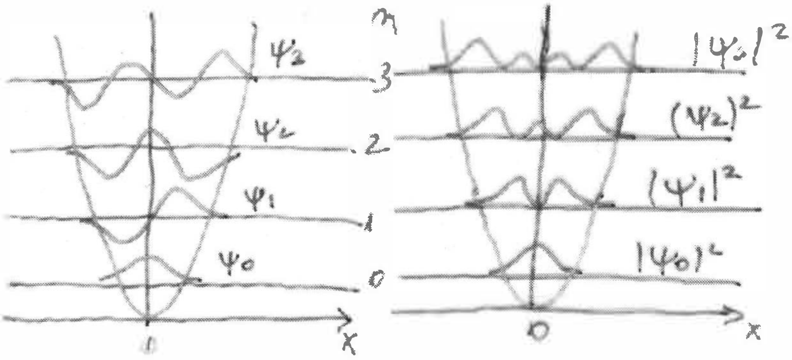
$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$n = 0, 1, 2 \ldots, \quad \omega = \sqrt{\frac{k}{m}}$$

$$\Delta E = E_{n+1} - E_n = \hbar\omega = h\nu$$



0-point energy $= \frac{1}{2}\hbar\omega$



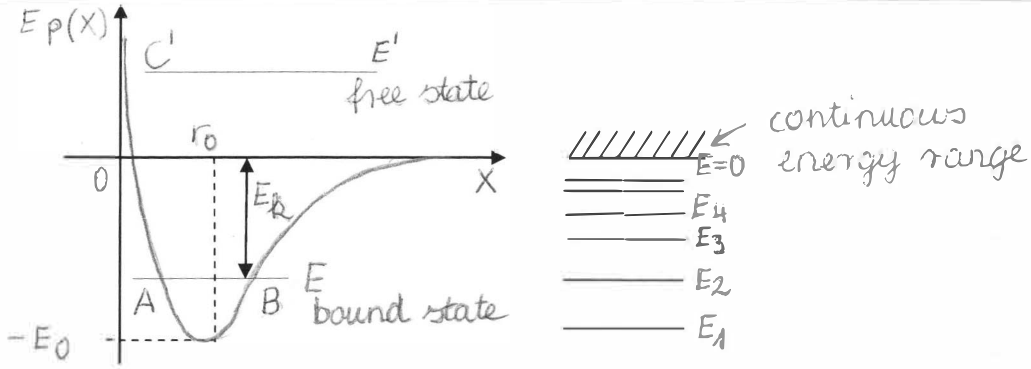
$|\psi|_3^2$ extends beyond the limits of classical motion but they decay rapidly.

In three dimensions: spatial harmonic oscillator

$$E_n = \left(n + \frac{3}{2}\right)\hbar\omega$$

- Real potential

E.g. central force



Large x → E_p = constant = 0

smaller x → E_p falls — attraction force

very small x E_p increases — repellent force

- Classically:

$E < 0 \rightarrow$ bound motion (oscillation between A and B)

$E > 0 \rightarrow$ reflection (C is point of return)

- Quantum mechanically

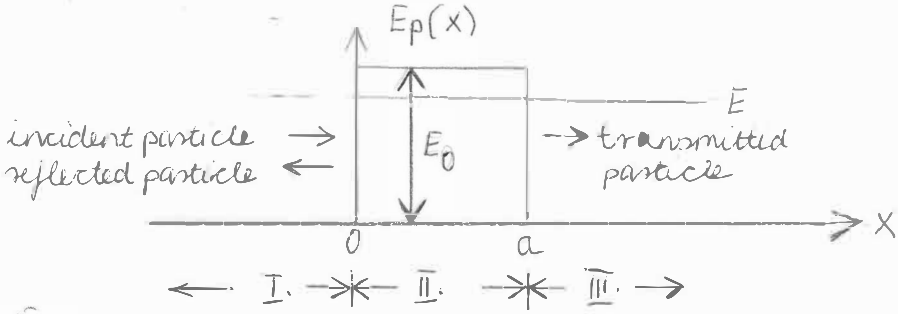
$E < 0 \rightarrow$ discreet solutions for bound states (discreet energy spectrum) 2 boundary conditions

$E > 0 \rightarrow$ only one boundary condition at C (continuous energy spectrum)

Binding energy $E_k \equiv$ energy needed to take the particle far ($E=0$) away from the bound state

Dissociation, ionization etc. energy

Transition through a potential barrier



- $E < E_0$

Classically: reflection

Quantum mechanically: partial transmission

For the ranges I, II and III the solutions of the Schrödinger eq.,

$$\psi_1 = Ae^{ikx} + Be^{-ikx}$$

$$\psi_2 = Ce^{\alpha x} + De^{-\alpha x}$$

$$\psi_3 = A'e^{ikx}$$

A, B, C, D, A' from the boundary conditions

$$k^2 = \frac{2mE}{\hbar^2}$$

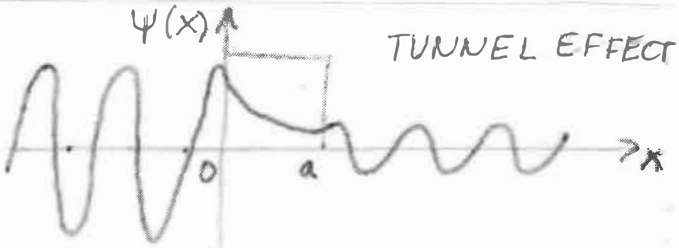
$$\alpha^2 = 2m\frac{(E_0 - E)}{\hbar^2}$$

Since at $x = 0$ ψ_2 is non-0 $\rightsquigarrow$

$\psi_3 \neq 0$

particle is transmitted

TUNNEL EFFECT



- $E > E_0$

Unlike classically there is reflection, too.

At discreet energies no reflection: resonance transmission

Condition: for the wavelength of the particle above the barrier

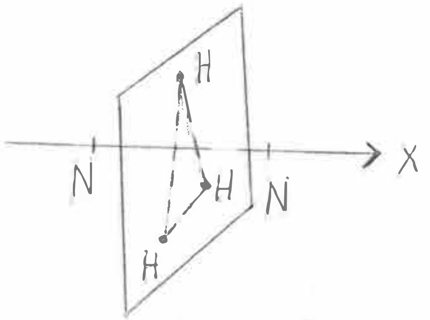
$$\lambda' = \frac{2\pi}{k'} \quad \text{where} \quad k'^2 = \frac{2m(E - E_0)}{\hbar^2}$$

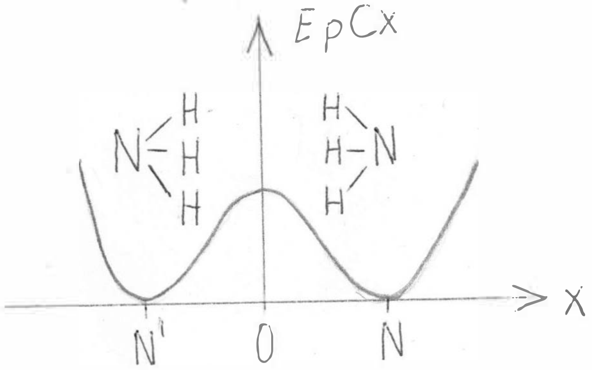
$$n \cdot \frac{\lambda'}{2} = a$$

must hold.

Examples

1. Inversion of the molecule ammonia NH_3





N atom has two symetric positions : 2 equivalent minima of potential energy

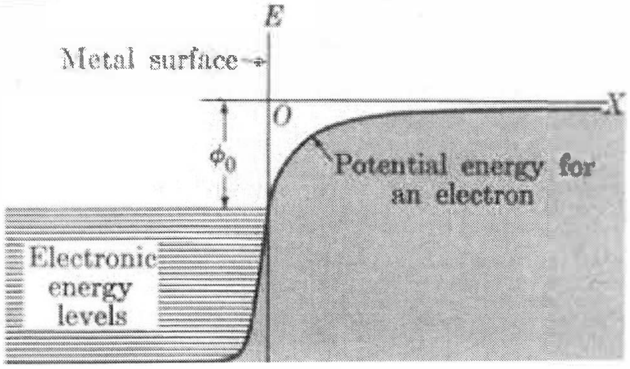
The motion is the superposita of 2 oscillation:

1. oscillation around N (or N')
2. slower oscillation between the two states crossing the potential barrier

NH_3 : $2,38 \cdot 10^{10}$ Hz

(time standard).

2. Emission of electron from metal



For emission energy $\geq \phi_0$ is required.

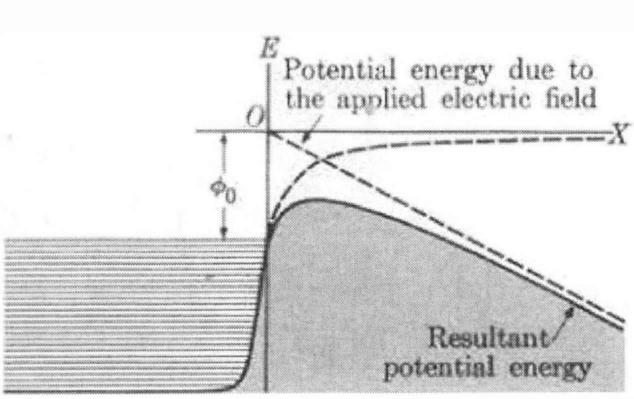
Energy feed:

heat – thermoemission

light – photoelectric effect

Other solution

With external electric field modification of the potential to a potential barrier



Electron emitted by tunneling:

field emission

(Cold cathodes)

Quantum mechanics / 4.

Time dependent Schr. eq.
Perturbation theory
Transition probability
Formal quantum mechanics
Measurement theory

- Time dependent Schrödinger eq.

Question : time dependence of φ

Formally: Schr.: $$\left.\begin{array}{l} -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}+E_p\Psi=E\Psi \\ \frac{p^2}{2m}+E_p=E \end{array}\right\} p=\frac{\hbar}{i}\frac{d}{dx}$$

Heisenberg's uncertainity principle

$$\left.\begin{array}{l} \Delta x\,\Delta p \geqslant \hbar \\ \Delta E\,\Delta t \geqslant \hbar \end{array}\right\} E=i\hbar\frac{\partial\Psi}{\partial t}$$

→ Time dependent Schr. eq.

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}+E_p\Psi=i\hbar\frac{\partial\Psi}{\partial t}$$

Not a wave equation (more like transport, but complex)

Solution : try seperation by space and time coordinates

$$\Psi(x,t)=\varphi(x)e^{-iEt/\hbar}$$

$$\frac{\partial\Psi}{\partial t}=-\frac{iE}{\hbar}\varphi(x)e^{-\frac{iEt}{\hbar}} \qquad \frac{\partial^2\Psi}{\partial x^2}=\frac{\partial^2\varphi}{\partial x^2}e^{-\frac{iEt}{\hbar}}$$

Substituting:

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi}{dx^2}+E_p\varphi=E\varphi$$

← stationary equation
~> E is the full energy

Since $\psi \sim e^{iEt/\hbar}=e^{i\omega t}$ the wavefunction oscillates with $\omega=\frac{E}{\hbar}$ (de Broglie!)

E.g.

- Particle moving to direction +x : $\varphi(x)=Ae^{ikx}$ ~>

$$\Psi(x,t)=\varphi(x)e^{iEt/\hbar}=Ae^{i(kx-\omega t)}$$ = wave moving in the +x direction

Phase velocity of the waves

$$v_{ph}=\frac{\omega}{k}=\frac{E}{p}$$

- Particle in a potential box:

$$\psi(x) = A \sin \frac{n\pi x}{a} = \frac{A}{2i}\left(e^{\frac{in\pi x}{a}} - e^{-\frac{in\pi x}{a}}\right)$$

$$\Psi(x,t) = A \sin \frac{n\pi x}{a}\, e^{-\frac{iEt}{\hbar}} =$$

$$= \frac{A}{2i}\left[e^{i\left(\frac{n\pi x}{a} - \frac{Et}{\hbar}\right)} - e^{-i\left(\frac{n\pi x}{a} + \frac{Et}{\hbar}\right)} \right]$$

Two counterpropagating waves → standing wave

The solutions $\psi(x,t) = \varphi(x)\, e^{-\frac{iEt}{\hbar}}$ are stationary since: $\Psi(x,t) = \varphi(x)\, e^{-\frac{iEt}{\hbar}}$

$$|\Psi(x,t)|^2 = \left[\varphi^*(x)\, e^{\frac{iEt}{\hbar}}\right] = \left[\varphi(x)\, e^{-\frac{iEt}{\hbar}}\right] = |\varphi(x)|^2$$

There exist non-stationary solutions as well!

It can be proven that those are linear combinations of the stationary states:

$$\Psi(x,t) = \sum_n C_n \varphi_n(x)\, e^{-\frac{iE_n t}{\hbar}}$$

E.g.:

$$\psi(x,t) = C_1 \varphi_1\, e^{-\frac{iE_1 t}{\hbar}} + C_2 \varphi_2\, e^{-\frac{iE_2 t}{\hbar}}$$

$$t=0: \ \psi(x,0) = C_1\varphi_1 + C_2\varphi_2$$

(← this and the normalization determines c_1, c_2)

The probability density

$$P(x,t) = |\psi(x,t)|^2 = |C_1\varphi_1|^2 + |C_2\varphi_2|^2 + $$

$$+ C_1 C_2^* \varphi_1 \varphi_2^*\, e^{-\frac{i(E_1-E_2)t}{\hbar}} + C_1^* C_2 \varphi_1^* \varphi_2\, e^{\frac{i(E_1-E_2)t}{\hbar}}$$

I.e. $P(x,t)$ oscillates with angular frequency

$$\omega = \frac{E_1 - E_2}{\hbar}$$

In general: the non-stationary states are the sums of states oscillating with $(E_n - E_{n'})/\hbar$ frequencies

This describes transitions between two stationary states of energy E_1 and E_2

In case of a charged particle, during the transition P oscillates with $\omega = (E_1 - E_2)/\hbar$ ~ emission or absorption of electromagnetic wave

$E_1 - E_2 = h\nu$ ⟹ Bohr equation

— Why does a system get into a non-stationary state?

Perturbation theory

E.g. Excitation of an electron of an atom
ground state → excited state transition
E_p = atomic potential + external perturbing potential

Schr. eq.: $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + (E_p + K)\psi = i\hbar\frac{\partial\psi}{\partial t}$

$K = K(t)$

Can be expanded into series by the powers of the perturbing potential energy

$K = 0$ $\quad \varphi_i e^{-\frac{i}{\hbar}E_i t}$ $\quad$ solutions (atomic wave-functions)

$\cdot K \neq 0$ $\quad \psi = \sum_r C_r(t)\varphi_r e^{-\frac{i}{\hbar}E_r t}$ $\quad$ we look for solution in this form

Substituting ψ into the Schr. eq., making use of that φ_r-s are orthonormal → set of equations for C_r-s

$$\frac{dC_k}{dt} = -\frac{i}{\hbar}\sum_r K_{kr} C_r e^{i\omega_{kr}t} \qquad K_r = \int \varphi_k K(t)\varphi_r \, dx$$

$$\omega_{kr} = \frac{E_k - E_r}{\hbar}$$

Solution: with successive approximation

⓴

n th approximation

$$C_k^{(n)}(t) = C_k^{(n-1)}(0) - \frac{i}{\hbar}\sum_r \int_0^t K_{kr}(\tau)\, e^{i\omega_{kr}\tau}\, C_r^{(n-1)}(\tau)\, d\tau$$

Weak perturbation : K appears at $t=0$ but the system is for some time in the vicinity of the initial state (i)

$$C_r^{(0)}(t) = \begin{cases} 1 & r = i \\ 0 & r \neq i \end{cases} = \delta_{ri}$$

$$C_k^{(1)}(t) = \delta_{ki} - \frac{i}{\hbar}\int_0^t K_{ki}(\tau)\, e^{i\omega_{ki}\tau}\, d\tau$$

Transition probability

$$W(i \longrightarrow k) = |C_k(t)|^2 = \frac{1}{\hbar^2}\left|\int_0^t K_{ki}(\tau)\, e^{i\omega_{ki}\tau}\, dt\right|^2 \qquad i \neq k$$

Depends on the " matrix element K_{ki}

When $K_{ki} = 0$ → forbidden transition (in 1st approximation)

Reason: it is against some conservation principle (e.g. angular momentum)

→ Selection rules

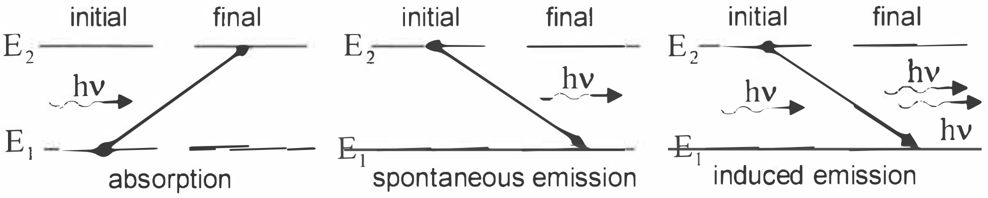
Higher order transitions → smaller probabilities

= Selection rules for a harmonic oscillator

$\Delta n = \pm 1$ absorption / emission at a single frequency

$\hbar\omega = E_{n+} - E_n$ = eigenfrequency of the oscillator

- Radiative transitions



Lifetime of excited state ~ $1/W(g \to \Sigma_i)$ all permitted transitions

atoms, molecules ~ 10^{-8} sec

nuclei : ~ $10^{-8} - 10^{-4}$ sec

Formal quantum mechanics

Schrödinger eq. → energy of the system only

Formal theory → how to get all the physical information about the system

Schr. eq.: $$\boxed{\left\{\frac{1}{2m}\left(-\hbar^2\frac{d^2}{dx^2}\right)+E_p(x)\right\}}\psi(x)=E\psi(x)$$

OPERATOR acting upon $\psi(x)$

(e.g. derivation, multiplication etc.)

$$\hat{H}=\frac{1}{2m}\left(-\hbar^2\frac{d^2}{dx^2}\right)+E_p(x)$$ Hamilton operator

$\hat{H}\psi(x)=E\psi(x)$ where $E=$ const. (The energy of the system)

↓

This equation holds only for selected $\psi(x)$ functions

These are the eigenfunctions of the $\hat{H}$ operator with E eigenvalues

For any operator

$\hat{A}\psi(x)=a\psi(x)$ eigenvalue equation →

$\{a_1, a_2, a_3 \dots\}$ and $\{\psi_1, \psi_2, \psi_3 \dots\}$

Set of eigenvalues and eigenfunctions

In quantum mechanics the operators representing physical quantities are Hermitian, i.e.:

$$\int\phi_1^*\hat{A}\phi_2\,d\tau=\int\left[\hat{A}\phi_2\right]^*\phi_1\,d\tau$$

Eigenvalues of Hermitian operators are real and their eigenfunctions are orthogonal.

$$\int\psi_i^*\psi_k\,d\tau=\delta_{ik}$$

(and form a complete set in the Hilbert space)

$\hat{H}$ – energy : (Hamilton operator

$H_{\text{classical}} = \frac{p^2}{2m} + E_p(X)$ full energy

In quantum mechanics $p \rightarrow \hat{p} = -i\hbar \frac{d}{dx}$

$$\hat{H}_{qu.m.} = \frac{\hat{p}^2}{2m} + E_p(X)$$

In 3 dimensions: $\hat{p}_x \rightarrow -i\hbar \frac{\partial}{\partial x}$ $p_y \rightarrow -i\hbar \frac{\partial}{\partial y}$ $p_z \rightarrow -i\hbar \frac{\partial}{\partial z}$

$$\hat{p} \rightarrow -i\hbar\left[\frac{\partial}{\partial x}\underline{u}_x + \frac{\partial}{\partial y}\underline{u}_y + \frac{\partial}{\partial z}\underline{u}_z\right] = -i\hbar\underline{\nabla}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\underline{\nabla}^2 + E_p(r)$$

I. To any $A(r,p)$ physical quantity there is a corresponding quantum operator with the replacement $\underline{p} \rightarrow -i\hbar\underline{\nabla}$ $A(\underline{r}, -i\hbar\underline{\nabla})$

Quantity	Classical def.	Quantum operator
position	$\underline{r}$	$\underline{r}$
momentum	$\underline{p}$	$-i\hbar\underline{\nabla}$
angular momentum	$\underline{r} \times \underline{p}$	$-i\hbar\,\underline{r} \times \underline{\nabla}$
kinetic energy	$\frac{\underline{p}^2}{2m}$	$-\left(\frac{\hbar^2}{2m}\right)\underline{\nabla}^2$
total energy	$\frac{\underline{p}^2}{2m} + E_p(r)$	$-\left(\frac{\hbar^2}{2m}\right)\underline{\nabla}^2 + E_p(r)$

II. When we measure the physical quantity $H(\underline{r}\,p)$ of the system, the measurement results can only be the eigenvalues of the $\hat{A}(\underline{r},-i\hbar\underline{\nabla})$ operator

$\hat{A}(r, -i\hbar\underline{\nabla})\psi = a\psi$ $a_1\ a_2\ a_3 \ldots$

$\psi_1\ \psi_2\ \psi_3 \ldots$

What happens when the system is not in an eigenstate of $\hat{A}$, i.e. $\phi \neq \psi_i$ (for all i)

~> A is indetermined — ϕ can be expanded.

$$\phi = \sum_n c_n \psi_n \quad \text{where} \quad c_n = \int_{\text{space}} \psi_n^* \phi \, d\tau$$

III. If the system is in state with wavefunction ϕ that is not an eigenstate of $\hat{A}$, then when we measure A, the probability of getting the result a_n is $|c_n|^2$ where $\int_{\text{space}} \psi_n^* \phi \, d\tau = c_n$ and ψ_n is the eigenvalue of $\hat{A}$ in state ψ_n

In such a ϕ state only the expectation value of A can be calculated

$$A_e = \int_{\text{space}} \phi^* \hat{A}(\underline{r}, i\hbar\underline{\nabla}) \phi \, d\tau =$$

$$= \int \phi^* \hat{A} \sum_n c_n \psi_n d\tau = \int \phi^* \sum_n c_n \hat{A} \psi_n d\tau =$$

$$= \int \phi^* \sum_n c_n a_n \psi_n d\tau = \sum_n c_n a_n \int \phi^* \psi_n d\tau =$$

$$= \sum_n c_n a_n c_n^* = \sum_n |c_n|^2 a_n$$

At each individual measurement we get one of the a_n eigenvalues, however the average of many measurements is A_e. ϕ contains all possible information about the system

IV. Evolution of a system in time is described

by $i\hbar \dfrac{\partial \psi}{\partial t} = \hat{H}\psi$ the time dependent Schrödinger equation

Matrix formalism

Eigenfunctions of $\hat{H}$ are $\psi_1, \psi_2, \psi_3 \ldots$ i.e. $\hat{H}\psi_n = E_n\psi_n$

Let A be another physical quantity with $\hat{A}$ operator

$A_{mn} = \int \psi_m^* A \psi_n \, d\tau$ → matrix elements

$$\begin{pmatrix} A_{11} & A_{12} & A_{13} \ldots \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \\ \vdots & & & \ddots \end{pmatrix}$$

E.g., matrix of $\hat{H}$ → $\begin{pmatrix} E_1 & 0 & 0 \ldots \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \ldots \\ \vdots & & \end{pmatrix}$

Because $H_{ij} (i \neq j) = \int \psi_i^* \hat{H} \psi_j \, d\tau = E_j \int \psi_i^* \cdot \psi_j \, d\tau = 0$

(normalization)

A state ⟺ state vector

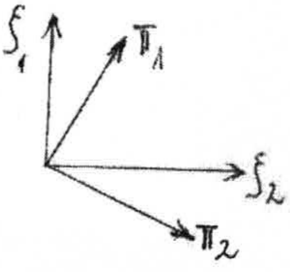
$\begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \end{pmatrix}$ State vector of a state with energy E_i $\begin{pmatrix} 0 \\ \vdots \\ \psi_i \\ \vdots \\ 0 \end{pmatrix}$

$$\begin{pmatrix} E_1 & & & \\ & E_2 & & \\ & & \ddots & \\ & & & E_i \end{pmatrix} \begin{pmatrix} 0 \\ \vdots \\ 0 \\ \vdots \\ \psi_i \end{pmatrix} = E_i \psi_i$$

E.g.: system with 2 states

$\hat{x}$ ξ_1 ξ_2 eigenfunctions $\begin{pmatrix} x_{11} & 0 \\ 0 & x_{22} \end{pmatrix}$

$\hat{p}$ in the system of ξ_1 and ξ_2 $\begin{pmatrix} p_{11} & p_{12} \\ p_{21} & p_{22} \end{pmatrix}$ $p_{ik} = \int \xi_i^* \hat{p} \xi_k \, d\tau$



ξ_1, ξ_2 are orthonormal eigenfunctions

Π_1, Π_2 can be expanded as linear combinations of ξ_1 and ξ_2 and vice versa

Measurement: measure x → let the system be in ξ_1 state

but $\xi_1 = a\Pi_1 + b\Pi_2$ ⇝ p is indefinite

probability of measuring $p_1 = \int \Pi_1^* \hat{p} \Pi_1 d\tau$ is $|a|^2$ and $|b|^2$ for p_2 for simultaneous measurement of x and p

→ Uncertainty relationship

There exist physical quantities with joint system of eigenfunctions $\uplus$ $\hat{H}\psi_i = E_i\psi_i$

E.g. energy $\hat{H}$ and angular momentum $\hat{L}\psi_i = L_i\psi_i$

Eigenvalues of $\hat{H}$ (E_i) can be degenerate → the same E_i corresponds to multiple $\psi_i^{(k)}$-s. (e.g. E_i in 3 dim)

Resolution of degeneracy: $\psi_i^{(k)}$-s differ in some other physical quantity (e.g. angular mom.) while the energy of these states is identical

$$\hat{L}\psi_i^{(k)} = l_i^{(k)}\psi_i^{(k)}$$

the system is characterised by the quantum numbers i, k

$\psi_i^{(k)} = \varphi_i\chi_k$ where φ_i and χ_k are the eigenfunctions of two operators of two different physical quantities ((i, k) → selected combinations only)

A real system: multiple quantum numbers

e.g. electron in a H atom $\psi_{n,l,m_l}^{(s)}$ 4 quantum nos

When measuring these quantities → eigenvalues

Other physical quantities – no joint set of eigenfunctions for individual eigenvalues probabilities only.

Operators with joint set of eigenfunctions: are commutative

$$[\hat{A},\hat{B}] = \hat{A}\cdot\hat{B} - \hat{B}\cdot\hat{A} = 0 \quad \text{i.e.} \quad [\hat{A},\hat{B}]\psi = 0\psi$$

For these quantities the uncertainity relationship ↓:

$$\Delta A \cdot \Delta B = 0$$

Non-commutative operators

$$\text{e.g. } (\hat{p}_x \cdot \hat{x} - \hat{x}\hat{p}_x)\psi = \left(-i\hbar\frac{\partial}{\partial x}x + i\hbar x\frac{\partial}{\partial x}\right)\psi =$$

$$= -i\hbar\left(\psi + x\frac{\partial\psi}{\partial x}\right) + i\hbar x\frac{\partial\psi}{\partial x} = -i\hbar\psi \neq 0$$

They do not have a joint set of eigenfunction ⇝ uncertainity relationship ↑: $\Delta x \cdot \Delta p_x \geq \hbar$

Angular momentum
Schröd.-eq. in a central force field
H atom, atoms with 1 elec

- Angular momentum

Electron in an atom: energy, momentum
are quantized
any other physical quantity?

Angular momentum $\underline{L} = \underline{r} \times \underline{p} = \underline{r} \times m\underline{v}$

In a central force field $\underline{L}$ is constant of motion
(no external torque!)

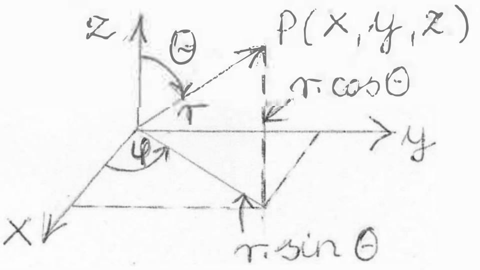
$\underline{L}$ is determined in quantum mechanics with L_z and L^2 (classically: direction and absolute value)

$$\hat{L} = -i\hbar\, \underline{r} \times \underline{\nabla} = -i\hbar \begin{vmatrix} u_x & u_y & u_z \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$$ (determinant

$$\rightarrow \hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$ $\hat{L}_x, \hat{L}_y$ similar

In spherical coordinates r, θ, φ

$x = r\sin\theta\cos\varphi$
$y = r\sin\theta\sin\varphi$
$z = r\cos\theta$



Let us write $\frac{\partial}{\partial\varphi}$ -

$$\frac{\partial}{\partial\varphi} = \frac{\partial x}{\partial\varphi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\varphi}\frac{\partial}{\partial y} + \frac{\partial z}{\partial\varphi}\frac{\partial}{\partial z}$$ but

$$\left.\begin{aligned} \frac{\partial x}{\partial\varphi} &= -r\sin\theta\sin\varphi = -y \\ \frac{\partial y}{\partial\varphi} &= r\sin\theta\cos\varphi = x \\ \frac{\partial z}{\partial\varphi} &= 0 \end{aligned}\right\} \begin{aligned} &\rightsquigarrow \frac{\partial}{\partial\varphi} = -y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y} \\ &\rightsquigarrow \hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi} \end{aligned}$$

$\hbar = 10^{-34}$ Jsec
(ang. mom.)

Eigenvalue equation

$\hat{L}_z\Psi = L_z\Psi \longrightarrow -i\hbar\frac{\partial\Psi}{\partial\varphi} = L_z\Psi$

with $\frac{L_z}{\hbar} = m_e \longrightarrow \frac{\partial\Psi}{\partial\varphi}\ im_e\Psi$

Solution: $\psi = C'e^{im_e\varphi}$

But $\varphi \to \varphi + 2\pi$ Ψ can not change ⇝

$e^{i2\pi m_e} = 1$ ⇝ $m_e = 0, \pm 1, \pm 2 \dots$ eigenvalues

From normalization: $C' = \frac{1}{\sqrt{2\pi}}$ ⇝

$\Psi(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im_e\varphi}$ and $L_z = m_e\hbar$ $\hbar = 10^{-34}$ Jsec (ang. mom.)

$\longrightarrow \hat{L}^2$?

$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$

In spherical coordinates

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

Eigenvalue equation:

$\hat{L}^2 Y(\theta,\varphi) = L^2 Y(\theta,\varphi)$ substituting

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} + \frac{L^2}{\hbar^2}Y = 0$$

Solution: eigenvalues: $L^2 = \hbar^2 l(l+1)$ $l = 0, 1, 2, \dots$

eigenfunctions: $Y_{e,m_e} = P_e^{m_e}(\cos\theta)e^{im_e\varphi}$

Y_{e,m_e} $\hat{L}^2$ and $\hat{L}_z$ Legendre polynom of l-th order

Y_{e,m_e} are joint eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$

$\hat{L}^2 Y_{l,m_e} = l(l+1)\hbar^2 Y_{l,m_e}$ $\hat{L}_z Y_{l,m_l} = m_l\hbar Y_{l m_l}$

In a Coulomb field

Let the energy quantum number be n ⇝

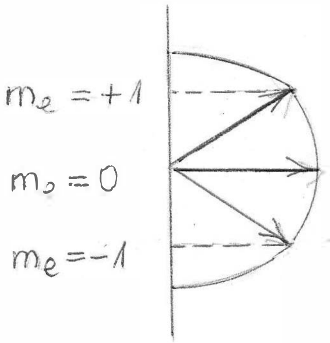
l can change between 0, ... (n−1)

The angle of the L vector with the z axis is discreet

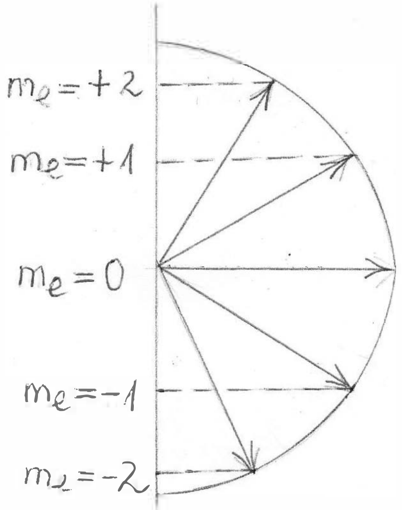
$L_z = m_l \cdot \hbar$

$m_l \le l$ for a given l

2l+1 different m_l-s $g = 2l+1$ = degree of degeneracy



$l = 1$
p



$l = 2$
d

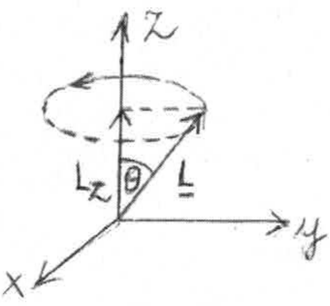
l =	0	1	2	3	4	5 ...
denotion	s	p	d	f	g	h
degree of degeneracy (2l+1)	1	3	5	7	9	11

Only one component of the angular momentum vector L can be measured precisely

If L_z is known $\Delta L_x \Delta L_y \ge \frac{\hbar}{2} L_z$

⇝ Direction of the angular momentum can not be precisely determined.

$|L|$ and L_z are determined
$\underline{L}$ is precessing around the z axes with a constant θ angle



The Schrödinger equation in a central force field

$E_p = E_p(\underline{r}) = E_p(r)$ Coulomb $E_p(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$

Schr. eq. $-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi + E_p(r)\psi = E\psi$

Transfer to spherical coordinates:

$$-\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\underbrace{\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]}_{\frac{1}{\hbar^2}\hat{L}^2}\right\}\psi + E_p(r)\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{\hat{L}^2}{\hbar^2 r^2}\right)\psi+E_p(r)\psi=E\psi$$

Eigenfunctions of $\hat{L}^2$

$\hat{L}^2\, Y_{l,m_l} = l(l+1)\hbar^2\, Y_{l,m_l}$ using these

$\psi = R(r)\, Y_{l,m_l}(\theta,\varphi)$ we look for solutions in this form

Substituting

$$-\frac{\hbar^2}{2m}\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right]R+E_p(r)R=E\cdot R$$

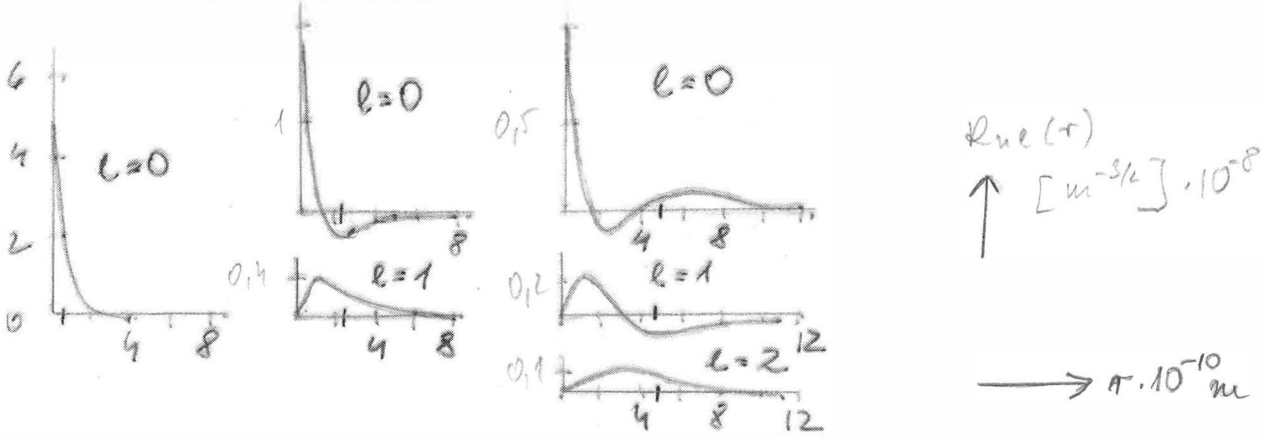
$R(r)$ is the radial part of the wavefunction

Trick: $R(r)=\frac{u(r)}{r} \rightarrow \frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[E_p+\frac{l(l+1)\hbar^2}{2mr^2}\right]u=Eu$

It is like a 1 dim. Schr. eq. $E_p^{eff}=E_p(r)+\underset{\uparrow}{\frac{l(l+1)\hbar^2}{2mr^2}}$

centrifugal potential

Radial part of the wavefunction (for a H atom) (real part)



s electrons ($l = 0$) can get very close to the nucleus

p, d less because l increases

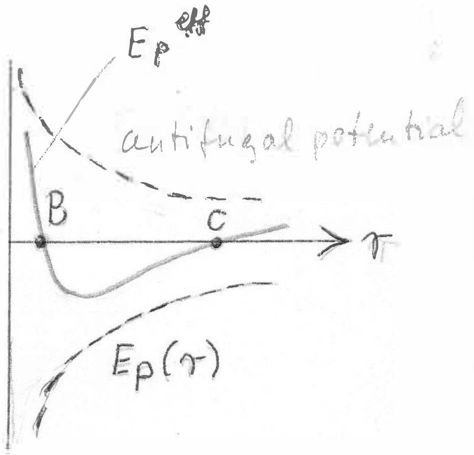
s orbit $l = 0$ $E_p^{eff} = E_p$ - attractive

Centrifugal potential : repellent

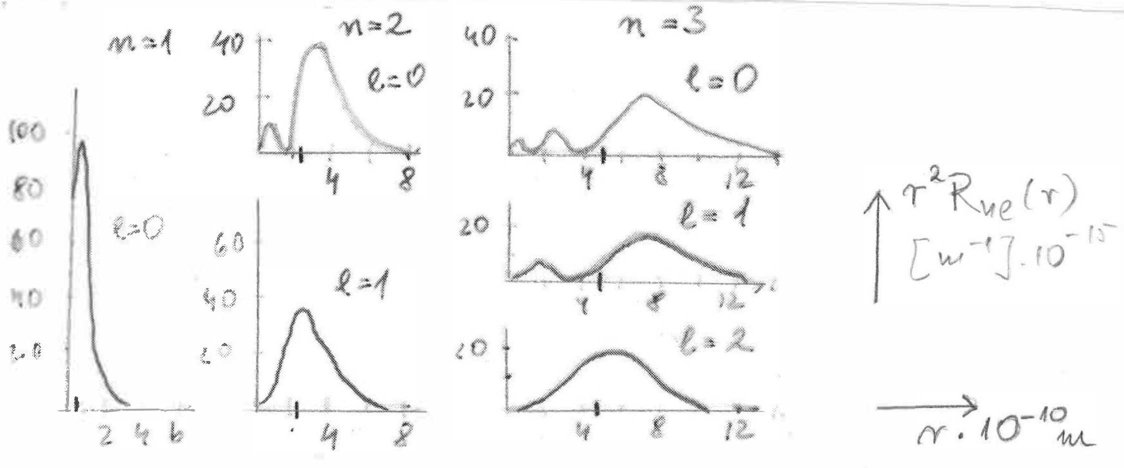
E_p^{eff} for $l > 0$ sum of the two

→ oscillation between B and C

(does not get closer than C)



Radial distribution of probability (for a H atom)



s electrons : sensitive to the internal structure of the nucleus

$l > 0$, p, d electrons : less sensitive

Atoms

size ~ 10^{-10} m (nucleus ~ 10^{-14} m)

– nucleus A (mass number) particles, of these

Z (atomic number) protons } nucleons
N = A − Z neutrons

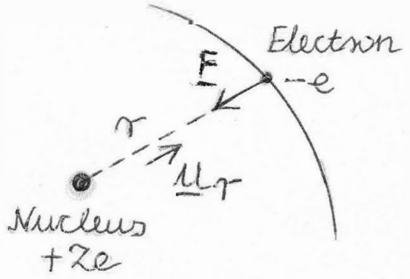
nuclear charge: +Ze

– Z electrons with charge −e } Electromagnetic interaction

– $m_{nucleon} \simeq 1850\, m_{electron}$

Atomic properties (eletromagnetic, elastic, etc.) are determined by the electrons

The Hydrogen atom



A = 1 , Z = 1

Assume: nucleus stationary
point like, charge Ze

Coulomb force: $\underline{F} = -\frac{Ze^2}{4\pi\varepsilon_0 r^2}\underline{u}_r$ $\rightsquigarrow$

The potential energy: $E_p(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$ $\rightsquigarrow$

Schrödinger equation:

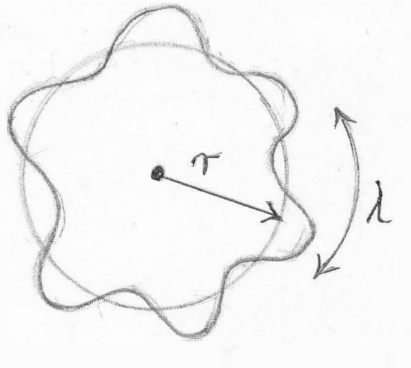
$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)-\frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

Looking for stationary states and their energies

Semiclassical approach (Bohr)

Analogous with the potential box

Electron → standing wave on a circular orbit



λ is the wavelength of the electron

$2\pi r = n\lambda$ for a standing wave

$r_n = \frac{n\lambda}{2\pi}$ $\quad L = r\cdot p = \frac{n\lambda}{2\pi}\frac{h}{\lambda} = n\cdot\hbar$ $\quad \left(p = \hbar k = \frac{h}{2\pi}\cdot\frac{2\pi}{\lambda} = \frac{h}{\lambda}\right)$

$\lambda = \frac{h}{p} \rightsquigarrow r \cdot p = L = \frac{nh}{2\pi} = n \cdot \hbar$ ang. mom.

Classically: centripetal force ≡ Coulomb attraction

$$\frac{m_e \cdot v^2}{r} = \frac{Z \cdot e^2}{4\pi\epsilon_0 r^2} \qquad p = m_e \cdot v = \frac{n\hbar}{r} \rightsquigarrow v = \frac{n\hbar}{m_e \cdot r}$$

$$\rightsquigarrow r = \frac{n^2 \hbar^2 \epsilon_0}{\pi m_e Z e^2} = \frac{n^2}{Z} \cdot a_0$$ a_0 = Bohr radius $= 5{,}3 \cdot 10^{-11}$ m

for the H atom $a_0 = r$ for $n = 1$ (ground state)

The energy of the electron

$$E = E_{kin} + E_{pot} = \frac{1}{2} m_e v^2 - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{1}{2} \frac{Ze^2}{4\pi\epsilon_0 r}$$

Substituting r

$$E = -\frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2 n^2} = -\frac{R_\infty h c Z^2}{n^2} = -\frac{13{,}6\, Z^2}{n^2} \, [eV]$$

R_∞ = Rydberg constant $(m_{nucl} = \infty) = \frac{m_e e^4}{8\epsilon_0^2 h^3 c} = 1{,}1 \cdot 10^7 \, m^{-1}$

Negative energies: bound states

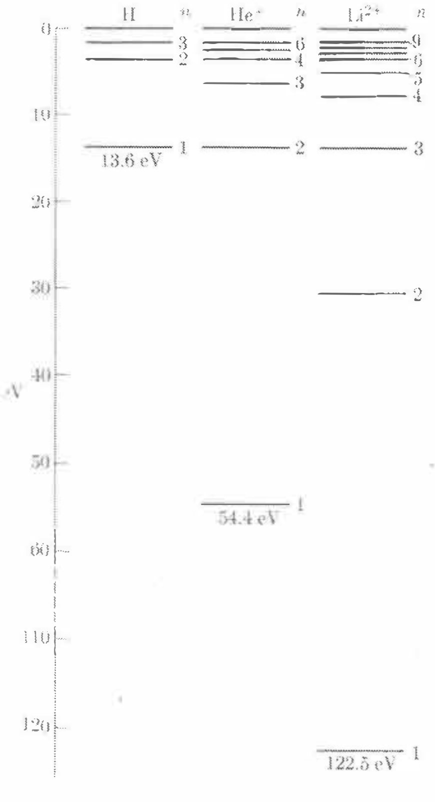
Certain levels coincide?

e.g. He^+ $n = 2, 4, 6$
Li^{2+} $n = 3, 6, 9$

No, because $m_{nucl} \neq \infty$

$$R = R_\infty \cdot \frac{\mu}{m_e}$$

$$\mu = \frac{m_e \cdot M_{nucl}}{m_e + M_{nucl}}$$ = reduced mass



Ionization energies!

Spectrum of the hydrogen atom

Measurement of radiation spectra: spectrometers

Energy differences between stationary energy states:

$$E_2 - E_1 = \left(-\frac{RhcZ^2}{n_2^2}\right) - \left(-\frac{RhcZ^2}{n_1^2}\right) = RhcZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Bohr: $\nu = \frac{E_2 - E_1}{h}$ for the emitted or absorbed radiation

$$\nu = \frac{E_2 - E_1}{h} = RcZ^2\left(\frac{1}{m^2} - \frac{1}{n_2^2}\right) = 3{,}3 \cdot 10^{15} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) [Hz]$$

This is the Balmer formula

Spectroscopy $\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$ wavenumber $[cm^{-1}]$

$$\tilde{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 10^5 Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) [cm^{-1}]$$

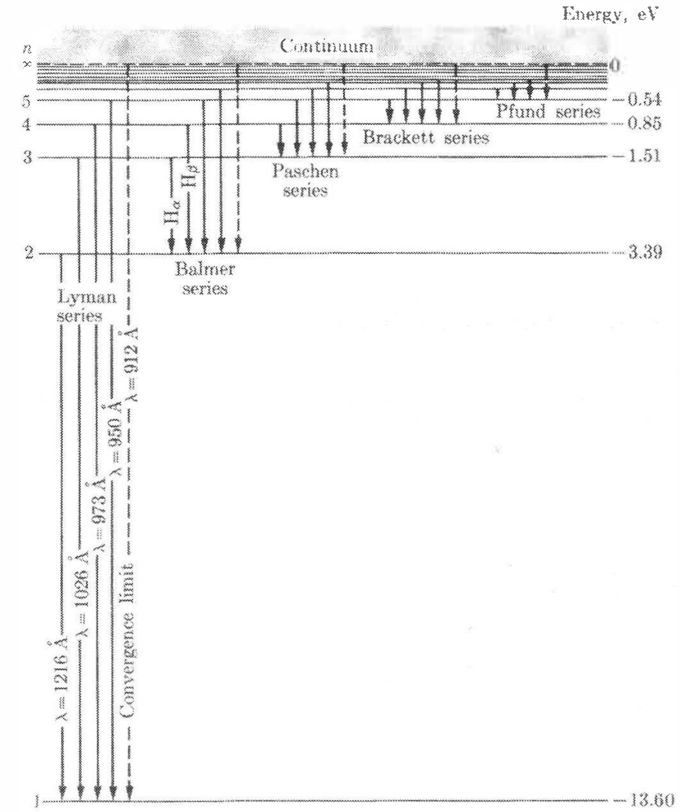
Spectral lines

Series: joint lowest energy states

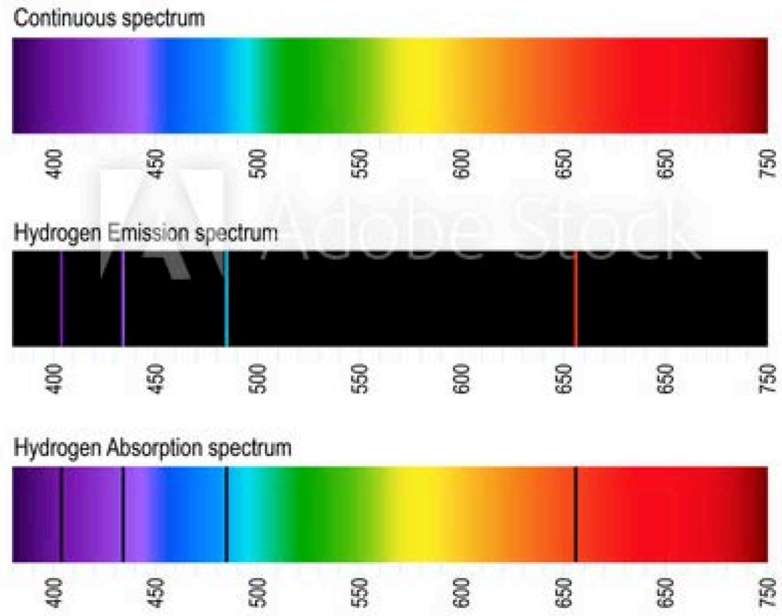
Balmer series: visible

Lyman series: UV

others: infra



SPECTRUM


Continuous spectrum
400
450
500
550
600
650
650
750
Hydrogen Emission spectrum
400
450
500
550
600
650
650
750
Hydrogen Absorption spectrum
400
450
500
550
600
650
650
750

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size ~ 10^{-10} m (nucleus ~ 10^{-14} m)

- nucleus A (mass number) particles, of these
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  - nuclear charge: +Ze > Electromagnetic interaction
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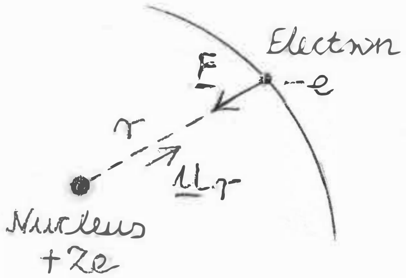

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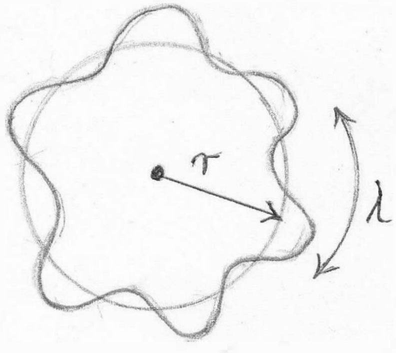
Semiclassical approach (Bohr)

Analogous with the potential box

Electron → standing wave on a circular orbit



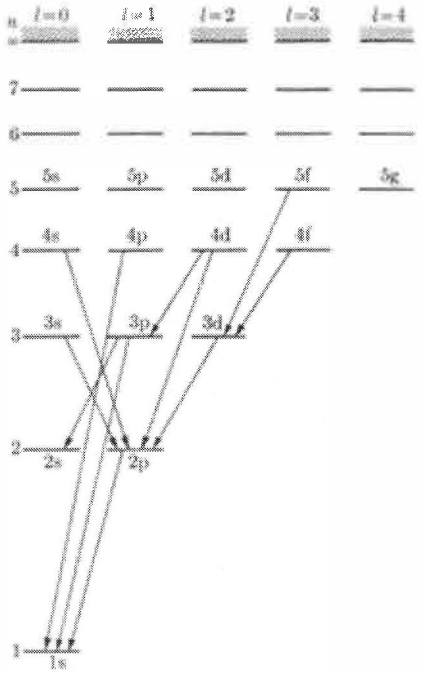
λ is the wavelength of the electron

$2\pi r = n\lambda$ for a standing wave

$r_n = \frac{n\lambda}{2\pi}$ $\quad L = r\cdot p = \frac{n\lambda}{2\pi}\frac{h}{\lambda} = n\cdot\hbar$ $\quad \left(p = \hbar k = \frac{h}{2\pi}\cdot\frac{2\pi}{\lambda} = \frac{h}{\lambda}\right)$

H atom: quantum mechanical analysis

- State: characterized by multiple quantum numbers n, l, m_l
- For given n
  l is between $0 - (n-1)$
  $\rightarrow n$ states with different l-s
- ns, np, nd states ($l = 0, 1, 2$) with the same energy
  (for $F \propto \frac{1}{r^2}$ only)
- In other central potentials: energy depends on n and l but not on m_l (direction)



Selection rules $\Delta l = \pm 1$ Δm_l

because of conservation of angular momentum

Angular momentum of the photon $= 1$

Metastable states (e.g. 2s) $2s \rightarrow 1s$ transition is forbidden (dipole approx.)

Orbit $\xrightarrow{q.m.}$ Wave function

Schrödinger equation in central force field

Shown earlier: $\psi(r, \theta, \varphi) = R(r) \cdot Y(\theta, \varphi)$

Due to the central symmetry $Y(\theta, \varphi)$ is identical for all central potential, determined by $|\underline{L}|$ and L_z

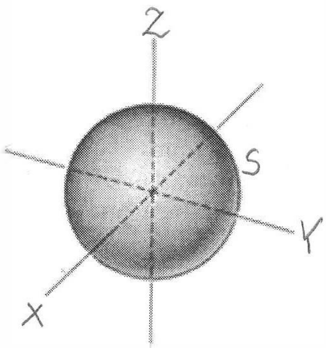
$l, m_l \rightarrow Y_{l, m_l}(\theta, \varphi)$ spherical harmonic functions

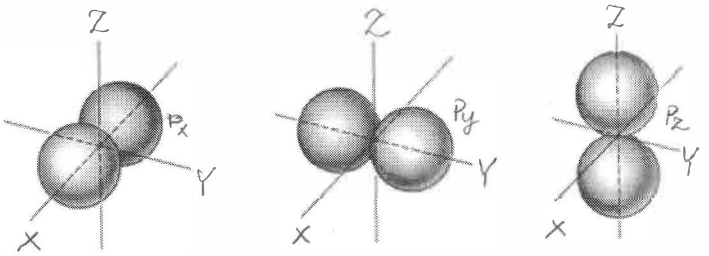
	l	m_l	$Y_{l,\,m_l}$
s	0	0	$Y_{00} = \frac{1}{\sqrt{4\pi}}$
p	1	0	$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$
		±1	$Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\varphi}$
d	2	0	$Y_{20} = \frac{1}{2}\sqrt{\frac{5}{4\pi}}(3\cos^2\theta - 1)$
		±1	$Y_{2\pm1} = \mp\sqrt{\frac{15}{8\pi}}(\sin\theta\cos\theta)e^{\pm i\varphi}$
		±2	$Y_{2\pm2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}(\sin^2\theta)e^{\pm i2\varphi}$

Ψ is the superposition of such directional (Y) and R radial distibutions

l larger → more complicated

$$\Psi_{n,l\,m_l}(r,\theta,\varphi) = $$
$$= R_{nl}(r)\, Y_{l\,m_l}(\theta,\varphi)$$

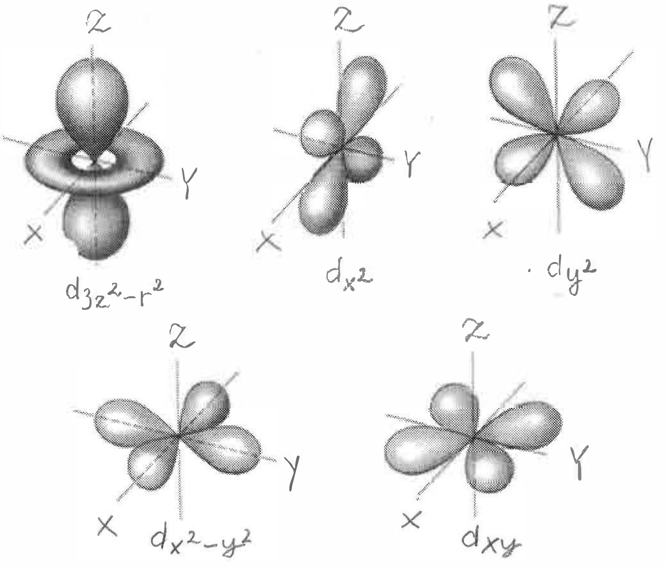




$|m_l| = 1$ $|m_l| = 1$ $|m_l| = 0$

p

Real parts
Eigenfunctions of l, and $|m_l|$



$|m_l|=0$

$|m_l| = 1$

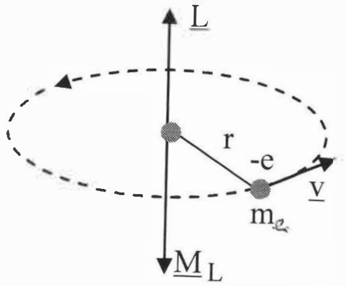
d

$|m_l| = 2$

Quantum mechanics / 6.

Zeeman effect
spin
total angular moment

Experiment: atomic spectral lines split into triplets in strong magnetic field



Zeeman effect

Charged particle + angular momentum → circular current → magnetic dipole moment

$$\underline{L} = m_e \cdot \omega r^2$$

$$M_L = (\text{circ. current})\cdot(\text{enclosed area}) = \frac{e}{T_{rot}} \cdot r^2\pi$$

$$= \frac{e\omega}{2\pi} r^2\pi = \frac{1}{2} e\omega r^2 = \frac{e}{2m_e} L$$

Due to the negative electron charge:

$$\underline{M_L} = -\frac{e}{2m_e}\underline{L}$$

z component of the magnetic moment

$$M_{L_z} = -\frac{e}{2m_e} L_z = -\frac{e\hbar}{2m_e} m_\ell = -\mu_B m_\ell$$

μ_B = Bohr magneton = $\frac{e\hbar}{2m_e} = 9{,}3\cdot 10^{-24}\,\mathrm{J}\,\mathrm{T}^{-1}$

Atom in an external $\underline{B}$ magnetic field receives magnetic energy $E_B = -\underline{M}\cdot\underline{B} = \frac{e}{2m_e}\underline{L}\cdot\underline{B}$

Let the z axe~~x~~ be ∥ with $\underline{B}$

$E_B = \mu_B \cdot B \cdot m_\ell$ where $B = |\underline{B}|$

But for an orbital with given ℓ → $2\ell+1$ different m_ℓ's

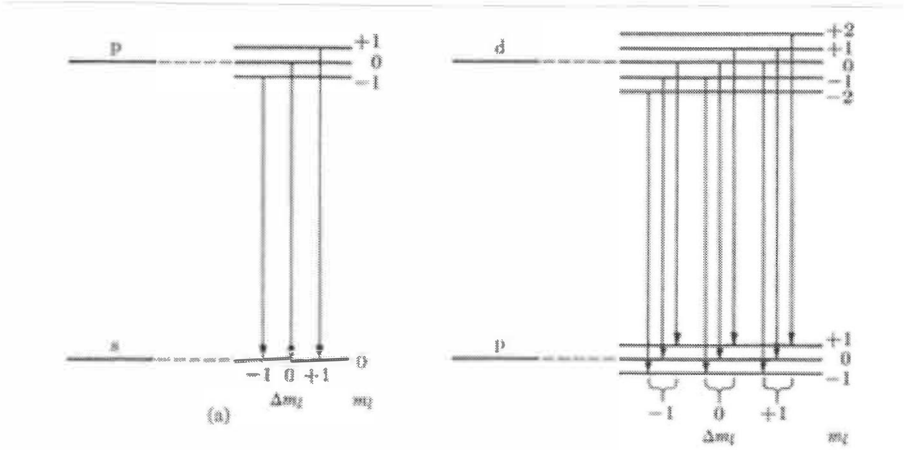
→ $2\ell+1$ different discreet E_B values

(corresponds to $2\ell+1$ different orientations of $\underline{L}$ relative to $\underline{B}$)

Energy of the electron

$E = E_n + E_B$

⇝ ∀ (n, l) level splits into $(2l+1)$ levels with different energies



- p state : $l = 1$ $m_l = +1, 0, -1$ 3 levels - triplet

p - s transition : triplet /3 lines)

$m_l = 0 \longrightarrow m_l = 0$ with the original frequency

$m_l = \pm 1 \longrightarrow m_l = 0$ $\nu + \Delta\nu$

$$\Delta\nu = \pm \frac{\mu_B \cdot B}{h} = 1{,}4 \cdot 10^{10} B \ [Hz]$$

- d state: $l = 2$ $m_l = 0, \pm 1, \pm 2$ 5 levels

but selection rule : $\Delta m_l = 0, \pm 1$!.

d - p transition 9 possibilitées, but when Δm_l is identical $\Delta\nu$ is the same

Δm_l can be $0, \pm 1$ only → triplet /3 lines/

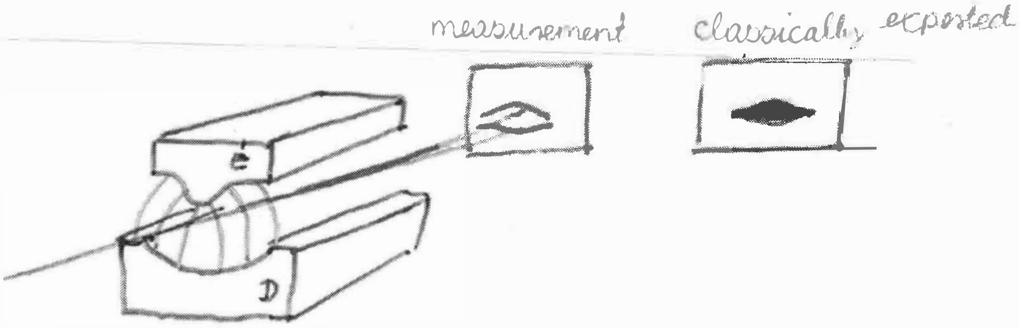
The Zeeman effect is the experimental proof of the quantization of the angular momentum.

/If $\underline{L}$ was a continuous variable it could stand at arbitrary direction relative to $\underline{B}$ instead of splitting → broadening would be observed in an external magnetic field/

Electron spin

Stern - Gerlach experiment:

In an inhomogeneous magnetic field H-like atoms (with s electron ground states: $l = 0$) for which $\underline{M}_L = 0$, deviate ⇝ They posess an inherent magnetic moment, $\underline{M}_s$



$|\underline{B}|$ increases toward the north pole $\quad \underline{F} = \mathrm{grad}(\underline{M} \cdot \underline{B})$

Magnetic dipole: if $\underline{M} \uparrow\uparrow \underline{B}$ → shifted toward increasing $|\underline{B}|$

if $\underline{M} \uparrow\downarrow \underline{B}$ → " " decreasing $|\underline{B}|$

Measurement → 2 kinds of dipole moments ⇝

The inherent magnetic moment of the electrons is also quantized $\underline{M}_s$

$\underline{M}_s$ is associated with angular momentum $\underline{S}$ ≡ spin

spin: 2 states $\quad (2s+1) = 2 \quad ⇝ \quad s = \frac{1}{2}$

$$\underline{M}_s = -g_s \frac{e}{2m_e} \underline{S} \qquad g_s = \text{gyromagnetic factor} = 2$$

The total magnetic moment

$$\underline{M} = \underline{M}_L + \underline{M}_s = -\frac{e}{2m_e}(\underline{L} + g_s \cdot \underline{S})$$

The 2 states of electronspin are parallel or antiparallel with the magnetic field

For the angular momentum

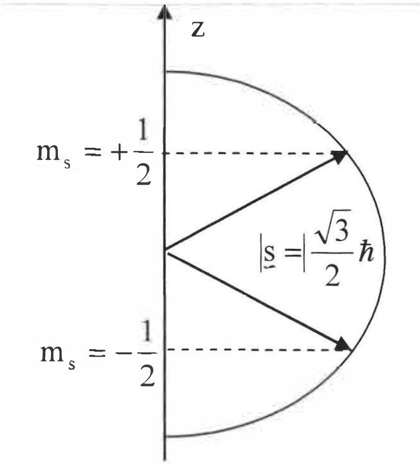
l given $\rightarrow$ $2l+1$ different directions

For the spin

2 directions $\rightsquigarrow$ $l = \frac{1}{2}$

quantum numbers: s, m_s $\rightarrow$ $s = \frac{1}{2}$ $m_s = \pm\frac{1}{2}$

Spin $\rightarrow$ physical quantity $\rightsquigarrow$ operator $\hat{\underline{s}}$



$s^2 = s(s+1)\hbar^2 = \frac{3}{4}\hbar^2$ $s = \frac{1}{2}$

$s_z = m_s \hbar$ $m_s = \pm\frac{1}{2}$

Spin wavefunctions:

χ_{m_s}

$\hat{s}^2 \cdot \chi_{m_s} = \frac{3}{4}\hbar^2 \chi_{m_s}$ $\hat{s}_z \chi_{m_s} = m_s \hbar \chi_{m_s}$

χ_+ $m_s = +\frac{1}{2}$

χ_- $m_s = -\frac{1}{2}$

So the total wavefunction of an electron in an atom is

$$\Psi_{n,l,m_l,m_s} = R_{nl}(r) Y_{lm_l}(\theta, \varphi) \chi_{m_s}$$

For complete characterization of the electron in a central force field 4 quantum numbers are necessary

$$\Psi_{n,l,m_l,m_s} = R_{nl}(r)\, Y_{l,m_l}(\theta,\varphi) \cdot \chi_{m_s}$$

Complete description of electron spin $\rightarrow$ relativistically invariant quantum mechanics (Dirac)

Coupling of the orbital ang. momentum and spin

Total angular momentum

$\underline{J} = \underline{L} + \underline{S}$

Possible values of J (possible states)

Addition rules for angular momenta:

$\underline{J} = \underline{J}_1 + \underline{J}_2 \qquad J_z = J_{1z} + J_{2z} \rightarrow$

$J^2 = j(j+1)\hbar^2 \qquad J_z = m\hbar \qquad m = \pm j, \pm(j-1), \dots$

$m = m_1 + m_2$

But J_1 and J_2 can have different relative directions

J can have different values

j from $(j_1 + j_2)$ to $(j_1 - j_2)$

↓ parallel — antiparallel

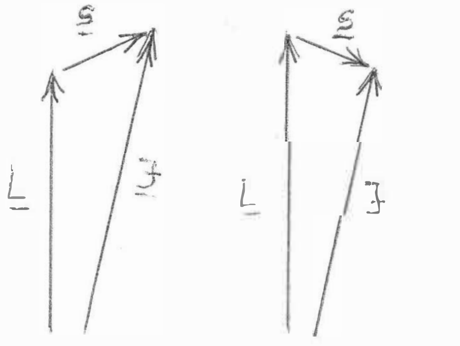
Orbital momentum and spin

$J_1 = \underline{L} \qquad J_2 = \underline{S}$

Possible values for $J = J_1 + J_2$

$j = l \pm \frac{1}{2}$ (when $l = 0$ $j = \frac{1}{2}$ possible only)

l	0	1		2		3	
j	1/2	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$	$\frac{7}{2}$
	$S_{1/2}$	$P_{1/2}$	$P_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$

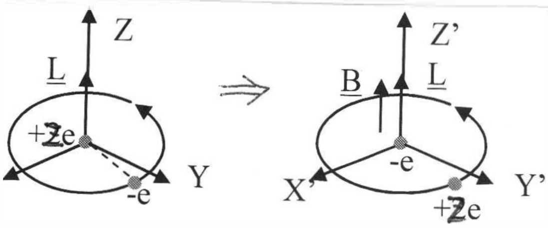


$j = l + \frac{1}{2}$ up $\qquad j = l - \frac{1}{2}$ down

Spin - orbit interaction

The spectral lines starting from the $l>0$ levels are doublets (e.g. D lines of Na /yellow/)

Connection with the 2 spin orientations?



From the coordinate system attached to the nucleus transfer to one attached to the "orbiting" electron (X', Y', Z') → the nucleus with charge $+Ze$ rotates around the electron → induces a magnetic field $\underline{B}$ ($\underline{B} \uparrow\uparrow \underline{L}$ since the charge is +)

In X', Y', Z' the electron is at rest → spin only

$\rightsquigarrow \underline{M}_s$ magnetic moment only $\underline{M}_s \parallel \underline{S}$

Interaction energy $\underline{M}_s \cdot \underline{B} \sim \underline{S} \cdot \underline{L}$

$E_{SL} = a \cdot \underline{S}\,\underline{L}$ Spin - orbit interaction

$E_{SL} \ll E_n$ (for normal energy levels)

$E = E_n + E_{SL} = E_m + a\,\underline{S}\,\underline{L}$

E_{SL} depends on the relative orientation of the two vectors → 2 possible states

Any state with a given l splits into 2 states (with small separation)

/except the s state/

$$j = l + \frac{1}{2}$$
$$j = l - \frac{1}{2}$$

In case of spin-orbit interaction the states are characterized by the following quantum numbers: l, j, m where m is the eigenvalue of j_z

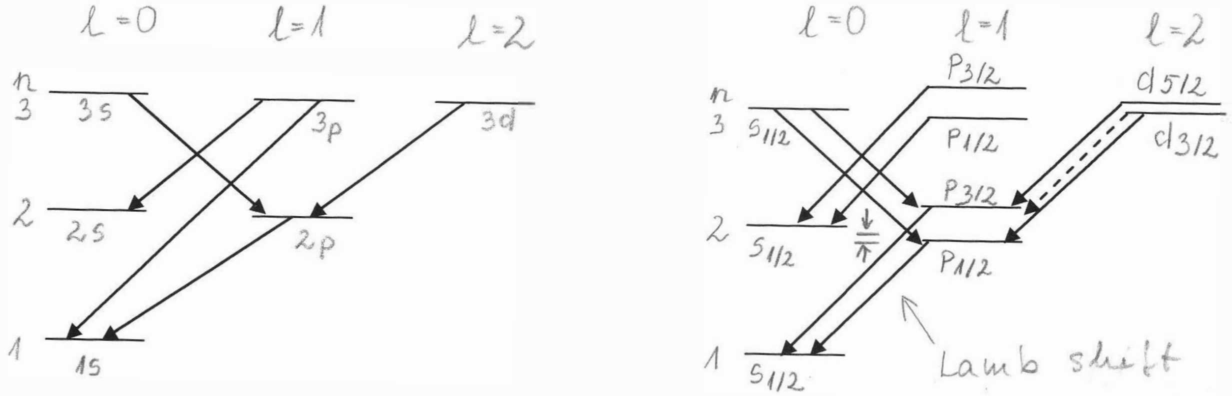
Selection rules for dipole transitions

$\Delta l = \pm 1 \quad \Delta j = 0, \pm 1 \quad \Delta m = 0, \pm 1.$

$\Delta j = 0$ is weak, since it requires simultaneously $\Delta l = \pm 1$ and $\Delta s = \mp 1$ (low probability)

The spectrum of the H atom changes accordingly

Without LS interaction With LS interaction



$\Delta l = \pm 1 \quad \Delta m_e = 0, \pm 1$

(Splittings in the figure are not to scale)

E.g. $\nu_{2p \to 1s} = 2{,}47 \cdot 10^{15}$ Hz

$\Delta\nu = \nu_{2p_{3/2} \to 1s_{1/2}} - \nu_{2p_{1/2} \to 1s_{1/2}} = 1{,}11 \cdot 10^{10}$ Hz

Fine structure of the spectrum

Identical j but different l: small shift $\sim 10^{-1}$ fine stucture

↑

Lamb shift

Atoms / I.

Helium atom
The exclusion principle

Atoms with multiple electrons

$$E_p = \sum_{\forall \text{ Electron}} \left(- \frac{Ze^2}{4\pi\varepsilon_0 r_i} \right) + \sum_{\substack{\forall \text{ pair of} \\ \text{electrons}}} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

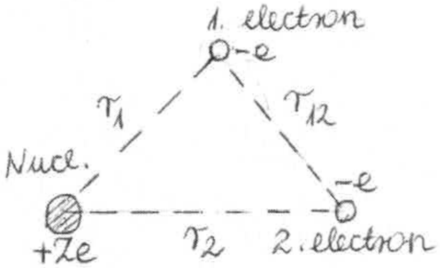
The electrons are not independent → interact

Approximate solutions only

The Helium atom

$\boxed{\text{He, } Z=2}$ H$^-$, $Z=1$ Li$^+$ $Z=3$

$$E_p = -\frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$



1. approximation: 3. term (~~electron~~-electron interaction) independent particle model

$$E_n = -\frac{13{,}6\,\text{eV}\, Z^2}{n^2}$$

H-like wavefct. ψ_{n,l,m_l} for both electrons

Energy of the groundstate: $E_{He} = -2 \frac{\overset{13{,}6\text{ eV}}{\boxed{Rhc}} Z^2}{1^2} = -109\,\text{eV}$

Experimentally $E_{He} = -79\,\text{eV}$

Because e-e interaction was neglected (repulsion: + energy)

2. approximation: interaction considered as <u>perturbation</u>

the electron moves in the field of the nucleus and the average (central) field of the 2. electron

⇝ 2. electron shields the charge of nucleus

$$E_{He} = -2 \frac{\overset{13{,}6\text{ eV}}{\boxed{Rhc}} (Z - S)^2}{1^2}$$

$\downarrow$

$-79\,\text{eV} \rightarrow S = 0{,}32$ shielding factor

Why?

- The possible electron states

1. Independent particle model

$\{n, l, m_l\} \longrightarrow a \qquad \{n', l', m_l'\} \longrightarrow b$

1. electron in state a
2. electron in state b

$\Big\} \rightarrow \psi_{atom} = \psi_a(1)\,\psi_b(2)$

$$|\psi_{atom}|^2 = |\psi_a(1)|^2 \cdot |\psi_b(2)|^2$$

2. Shielding potential perturbation

Assumed to be central $\mapsto \frac{1}{r}$ changes some ⤳

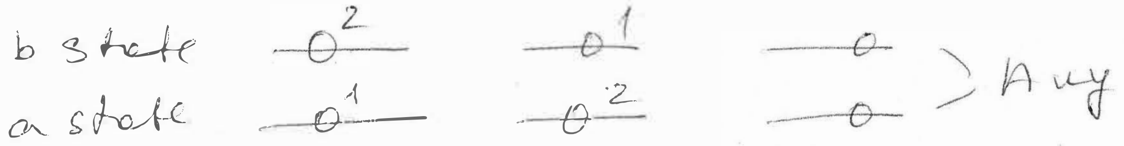
⤳ $R_{nl}(r)$ changes but Y_{l,m_l} is the same

<u>But</u> the electrons are <u>indistinguishable</u>!

States $\psi_a(1)\psi_b(2)$ and $\psi_a(2)\psi_b(1)$ must have the same energy

⤳ ψ_{atom} must reflect this symmetry, i.e.

$|\psi_{atom}|^2$ must not change when exchanging electron $1 \leftrightarrow 2$



$\psi = \quad \psi_a(1)\psi_b(2) \qquad \psi_a(2)\psi_b(1) \qquad \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) \pm \psi_a(2)\psi_b(1)\right]$

The symmetry requirement is fulfilled by the states

$$\psi_{atom} = \frac{1}{\sqrt{2}}\left[\psi_a(1)\,\psi_b(2) \pm \psi_a(2)\,\psi_b(1)\right]$$

Symmetric $\psi_S = [\quad + \quad] \qquad \psi_S(1,2) = \psi_S(2,1)$

Antisymmetric $\psi_A = [\quad - \quad] \qquad \psi_A(1,2) = -\psi_A(2,1)$

The energies of the symetric and antisymetric states are different.

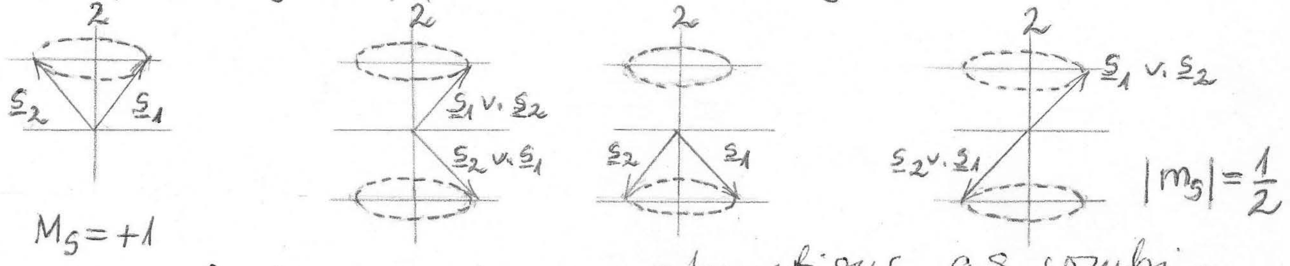
Reason: ψ_A assume the two electrons close in space their wavefunction would be very similar $\rightsquigarrow \psi_A = 0 \Rightarrow$ Therefore in ψ_A the electrons are further away → less interaction between them. Unlike for ψ_S where there is no such effect.

$\rightsquigarrow$ Sets of 2 stationary states and energy level systems
(except when $a = b \rightsquigarrow \psi_A = 0$, only $\psi_S\ \exists$)

Spin: was not included in "a" and "b"

There may be two $s = \frac{1}{2}$ spin electrons parallel $S = 1$ $(\frac{1}{2}, \frac{1}{2})$ or antiparallel $S = 0$ $(\frac{1}{2}, -\frac{1}{2})$

triplet $M_S = +1, 0, -1$ singlet $M_S = 0$



The two electron spin wavefunctions as combinations of the on electron spin wavefuts. χ_+ ad χ_-

Singlet antisymetric $\chi_A = \frac{1}{\sqrt{2}}\left[\chi_+(1)\chi_-(2) - \chi_+(2)\chi_-(1)\right]$ $M_S = 0$

Triplet symmetric

$$\chi_S = \begin{cases} \chi_+(1)\chi_+(2) & +1 \\ \frac{1}{\sqrt{2}}\left[\chi_+(1)\chi_-(2) + \chi_+(2)\chi_-(1)\right] & 0 \\ \chi_-(1)\chi_-(2) & -1 \end{cases}$$

The total electron wavefunction of the atom =
(orbital wavefunction) x (spin wavefunction)

By spectral measurements (Ψ_s and Ψ_A have different energies)

Ψ_s (orbit) always singlet $\longrightarrow \chi_A$ is attached

Ψ_A (orbit) always triplet $\longrightarrow \chi_S$ — " —

Therefore:

The total wavefunction of the system of electrons is always antisymmetric

He : $S = 0$ parahelium /with singlet states/

$S = 1$ ortohelium /with trilet states/

Probability of transitions between triplet and singlet states is small → would require spin rearrangement/

He : mixture of two gases with ratio 1:3

The energies

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}$$

$$\hat{H}_1 = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1}$$

$$\hat{H}_2 = -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_0 r_2}$$

$$\hat{H}_{12} = -\frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$i = 1, 2$

$$\hat{H}_i \Psi_a(i) = E_a \Psi_a(i)$$

$$\hat{H}_i \Psi_b(i) = E_b \Psi_b(i)$$

$$(\hat{H}_1 + \hat{H}_2)\Psi = (E_a + E_b)\Psi$$

where $\Psi = \Psi_A$ or Ψ_S

Using the above:

The energy

$$E = \int \psi^* \hat{H} \psi \, d\tau = E_a + E_b + \underbrace{\int \psi^* \hat{H}_{12} \psi \, d\tau}_{\text{this must be calculated}}$$

$$\int \psi^* H_{12} \psi \, d\tau = C' \pm K \quad \begin{matrix} + \text{ symmetric} \\ - \text{ antisymmetric} \end{matrix} \quad \text{orbital wavefct.}$$

$$C' = \iint_{1\,2} \frac{e^2}{4\pi\varepsilon_0 r_{12}} |\psi_a(1)|^2 d\tau_1 |\psi_b(2)|^2 d\tau_2 \quad \text{Coulomb integral}$$

$$K = \iint_{1\,2} \frac{e^2}{4\pi\varepsilon_0 r_{12}} \psi_a^*(1)\psi_b(1)\, d\tau_1\, \psi_b^*(2)\psi_a(2)\, d\tau_2 \quad \text{Interaction integral}$$

$C \rightarrow$ interaction between $\varrho_1 = -e|\psi_a(1)|^2$ and $\varrho_2 = -e|\psi_b(2)|^2$

$K > 0$

$K \rightarrow$ —— " —— $\varrho_1' = -e\psi_a^*(1)\psi_b(1)$ and $\varrho_2' = -e\psi_b^*\psi_a(2)$

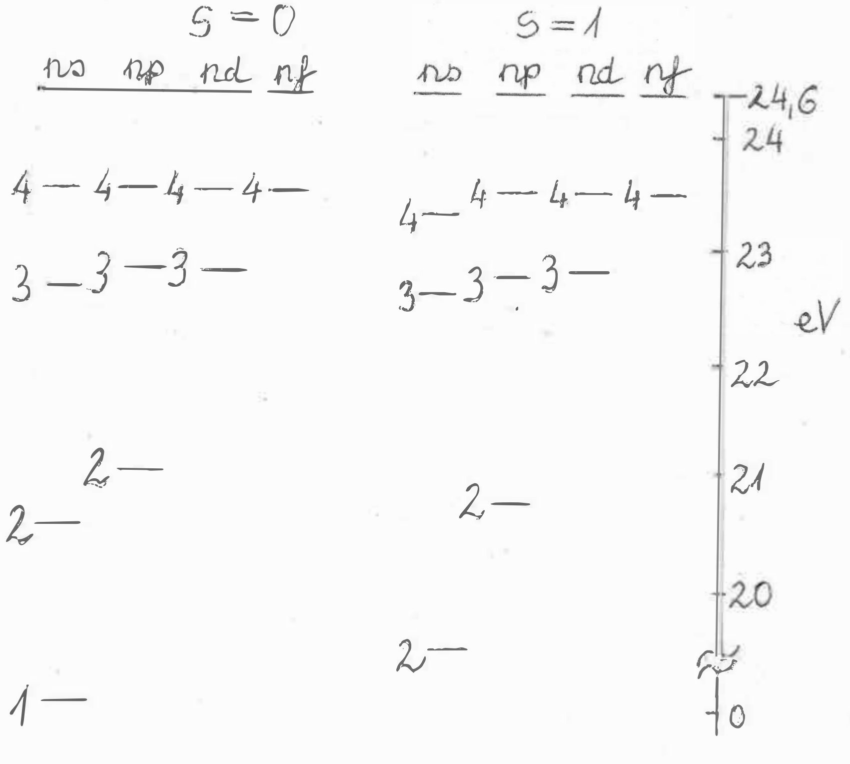
charge distributions

$$E = E_a + E_b + C' \pm K$$

$\rightsquigarrow$ For ψ_S /singlet/ $+K$ higher $\}$ $\rightsquigarrow$

ψ_A /triplet/ $-K$ lower

$2K$ energy difference between the energy levels of para- and orto-helium.



(1 of the electron in the 1s state)

$n=1$ for $S=0$ $\exists$ only, because $1s-1s$ is symmetric $\rightarrow \chi$ must be χ_A

The exclusion principle

Atom with multiple electrons

Each electron characterised by quantum numbers n, l, m_l, m_s

Energy: depends on n, l (ignoring spin-orbit interaction)

With given n, l: a certain number of "equivalent" electrons: these differ only in m_l and m_s

Pauli principle: In an atom all the quantum numbers of 2 electrons can not be identical

This is equivalent with the complete wavefunction of the system being antisymmetric

$$\begin{vmatrix} \psi_a(1) & \psi_a(2) \\ \psi_b(1) & \psi_b(2) \end{vmatrix} = \psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)$$ determinant for 2 electrons

An atom with N electron

$a = \{n, l, m_l, m_s\}$ $b = \{n', l', m_l' m_s'\}$ $c = \dots$

The wavefunction of the N electron system is

$$\psi_{abc\dots} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \psi_a(3)\dots \\ \psi_b(1) & \psi_b(2) & \psi_b(3)\dots \\ \psi_c(1) & \psi_c(2) & \psi_c(3)\dots \\ \vdots & & \vdots \quad \ddots \end{vmatrix}$$

$\psi_{abc\dots}$ is antisymmetric since exchange of 2 electrons $\equiv$ exchange of 2 colomns in the determinant → it changes sign

2 electrons with identical sets of quatum numbers

e.g. $a = b$ → 2 rows identical → determinant $= 0$

Conclusion: properties of multielectron systems: atoms, molecules, solids

Principle of antisymmetricity: electrons, protons, neutrons etc. ⇒ fermions

Atoms /2.

Electron structure of atoms
Valence electrons
X-rays

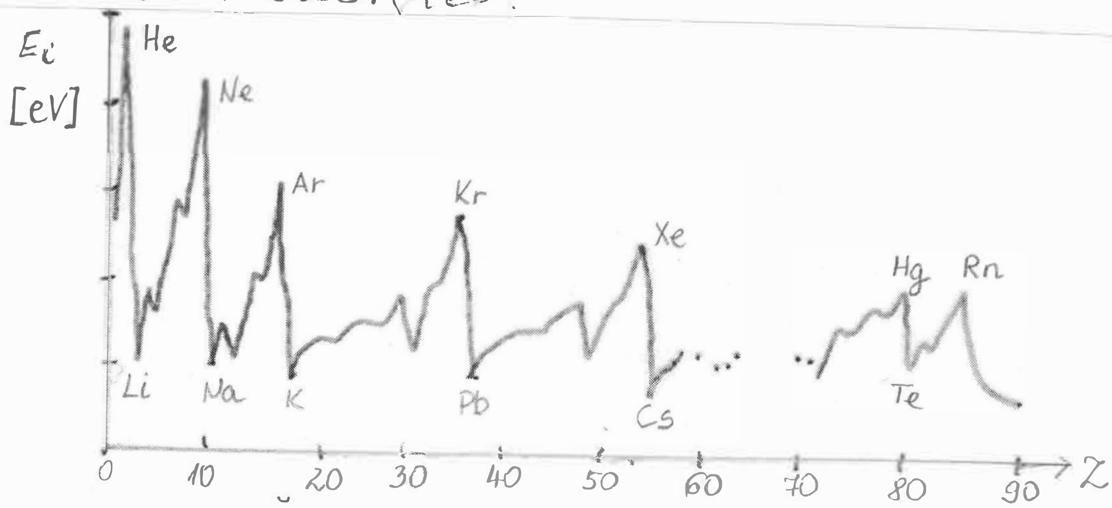
Electron structure of atoms

Independent particle model + Pauli principle

Elements: periodicities in the physical and chemical properties

Periods $Z = 2, 10, 18, 36, 54, 86$ He, Ne, Ar, Kr, Xe Rn

Ionization energies!



(deviation at transition metals, rear earth metals)

Question: for any n, l state how many m_l, m_s combinations? This gives for n, l state the maximum number of coexisting electrons

$\forall l \rightarrow 2(2l+1)$ kind of m_l and m_s $(m_s = \pm\frac{1}{2})$

$n, l \rightarrow 2(2l+1)$ electrons can coexist

configuration number $x = 2(2l+1)$

notation: nl^x e.g.: He ground state $1s^2$

Let us build up the atoms of the elements from $Z=1$

New electron is always added to the lowest energy state allowed by the exclusion principle

States with n, l filled – a shell is filled

Additional electron → to new shell

Shells: larger energy difference between them

Full shells:

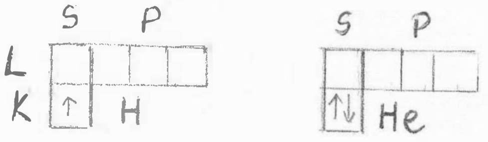
$Z = 2, 10, 18, 36, 54$

noble gases

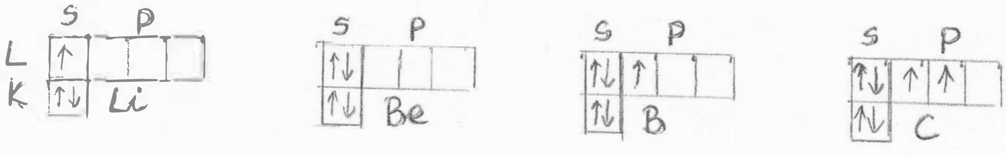
	s	p	d	f	g
$l =$	0	1	2	3	4
$2(2l+1) =$	2	6	10	14	18

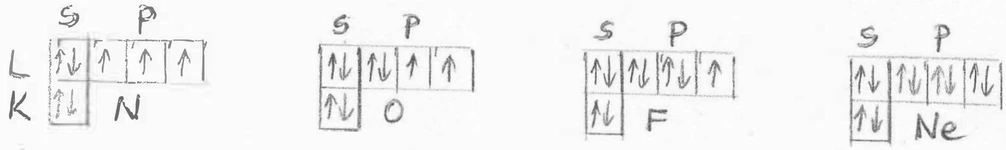
Levels	No. of electrons in the shell ($2(2l+1)$)		Shell completely filled
7p	6	32	118 (?)
6d	10		
5f	14		
7s	2		
6p	6	32	86 (Rn)
5d	10		
4f	14		
6s	2		
5p	6	18	54 (Xe)
4d	10		
5s	2		
4p	6	18	36 (Kr)
3d	10		
4s	2		
3p	6	8	18 (Ar)
3s	2		
2p	6	8	10 (Ne)
2s	2		
1s	2	2	2 (He)

Build up of the first 10 elements



$n = 1, 2, 3, 4 \ldots$
K L M N …





$K \rightarrow n=1 \rightsquigarrow l=0 \rightarrow s \qquad m_s = \pm \frac{1}{2}$

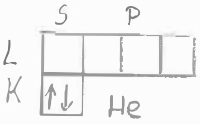
$L \rightarrow n=2 \rightsquigarrow l=0 \rightarrow s \qquad m_s = \pm \frac{1}{2}$

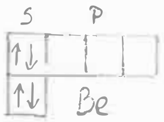
$l=1 \rightarrow p \qquad m_l = +1, 0, -1, \; m_s = \pm \frac{1}{2}$

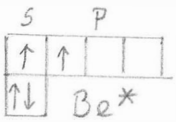
In the course of filling the shells: maximum number of parallel spins

Hund's rule: spin of the ground state of atoms is the maximum allowed by the exclusion principle

Reason: ground state ↔ small repellence between the electrons
⇒ antisymmetric orbital wavefunction
⇒ spin wavefunction is symmetric





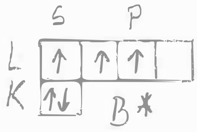


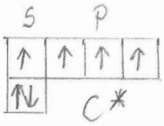
He and Be: completely filled 1s and 2s levels

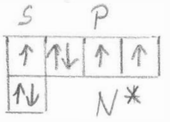
He - noble gas Be - is not

Reason: One of the 2s electrons of Be can be easily excited to the 2p level close in energy (differing only due to fine structure

Be* → 2 uncompensated spins
valence = 2







Physical and chemical properties of atoms are determined by the ~~ground~~ electron configurations of the ground state and the closely lying excited states.

E.g.: noble gases: filled shells
large energy difference to the next unfilled energy state.

closed (filled) shell + 1e
e.g. Li, Na, K
the outermost electron is only loosely bound
metallic behaviour

L-S coupling

Complete angular momentum of multielectron atoms

Selection rules

Isolated atom: total angular momentum J = constant

$J^2 = J(J+1)\hbar^2$ $\quad J_z = M\cdot\hbar \quad M = \pm J, \pm(J-1)\ldots$

To any given electron configuration: many J-s

(many different wavefunctions and energies)

L-S or Russel-Sounders coupling

Full wavefunction is antisymmetric

individual electrons: n, l, m_l, m_s

$\underline{L} = \sum_i \underline{L}_i \quad L_z = \sum_i L_{zi}$

$L^2 = L(L+1)\hbar^2 \quad L_z = M_L\cdot\hbar \quad M_L = \pm L, \pm(L-1)$

Similarly for the spin

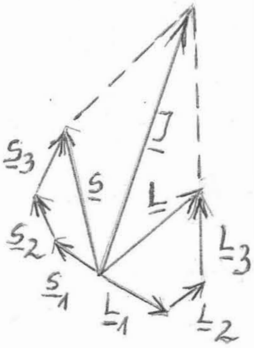
$\underline{S} = \sum_i S_i \quad S_z = \sum_i S_{zi}$

$S^2 = S(S+1)\hbar^2 \quad S_z = M_S\hbar \quad M_S = \pm S, \pm(S-1)$

The total angular momentum:

$\underline{J} = \underline{L} + \underline{S} \qquad J = L+S, L+S-1, \ldots |L-S|$

e.g. for a 3 electron atom →



In case of the same $\{n_i\}$ configuration different $\underline{L}$ and $\underline{S}$ are possible

different energies due to different relative orientations of the motion of the electrons (Coulomb interact.) ⇒ Complicated energy level structure

For given L & S → different $\{n_i\}$-s (terms)

For given L & S but different J → slightly different energies only (due to spin-orbit interaction)

Valence electrons

Completely filled shells form a "kernel": the external electrons feel the nuclear charge shielded by the kernel

For the kernel $L=0$, $S=0$

External electrons → valence electrons → they determine the behaviour of the atoms

Excitations: primarily the valence electrons

- 1 valence electron

e.g. Li $Z=3$

kernel: 2 electrons + 1 valence electron

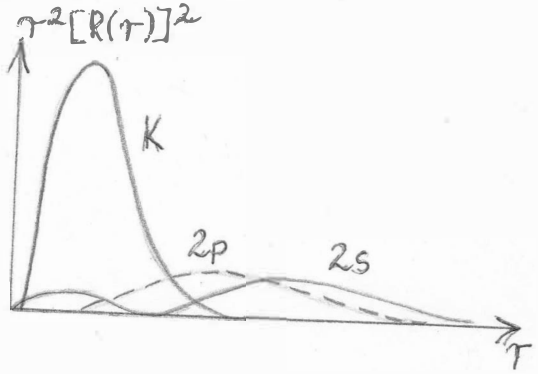
The shielding effect of the kernel depends on the orbit (state) of the valence electron

First approxim.: $+3e$ nuclear charge

$-2e$ kernel -"-

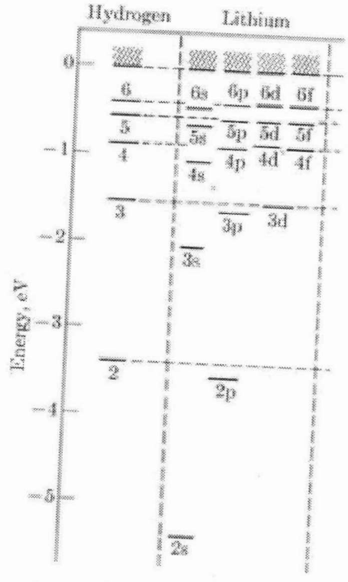
$+e$ effective charge

H-like



But for the states with small l the valence electrons penetrates the kernel → The energies depend on l!

When n and l are large less penetration more H-like levels



- 2 valence electrons.

He like energy levels

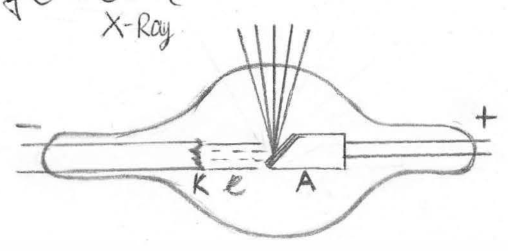
e.g. Be, Mg, Ca

Two groups of energy levels $S=0$ siplet, $S=1$ triplet

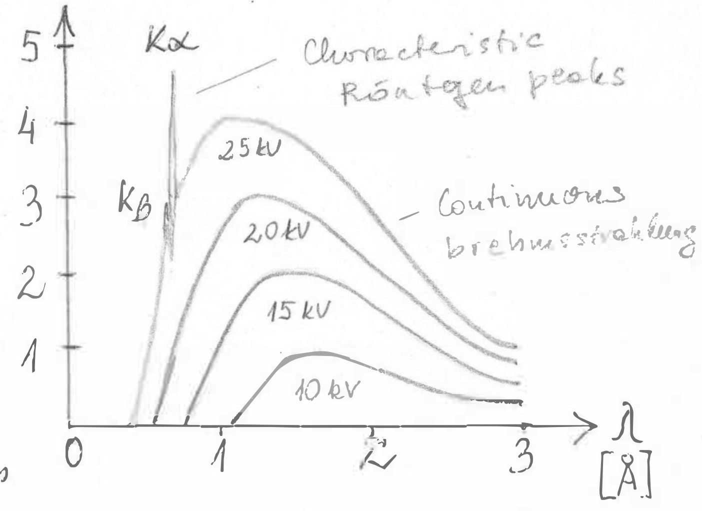
Strong l dependence

X-rays (Röntgen)

Based on exitation of electrons in the completely filled kernel



Radiation spectrum for Molibdenium anode at different accelerating voltages →



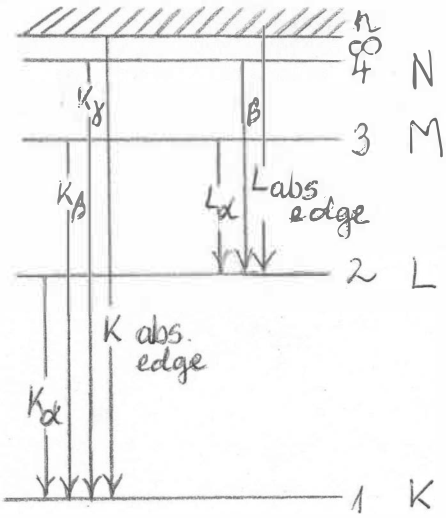
K series excitation potential > 20,0 kV

Sharp peaks: λ peak depends on the anode material

Accelerated electron collides with the atoms of the electrode knocks out an electron from the kernel
e.g. from the K shell (n=1) — an empty state (so called "hole") remains

From a higher energy level (from the shell, or a valence electron, or a free electron) falls into the hole

From the L, M, N shell → Kα, Kβ, Kγ



X ray spectrum
It can be generated by creation of a "hole", otherwise no electron can return to a closed shell due to the exclusion principle

Fine structure → the l of the kicked out electron

— Auger effect: the generated X ray does not exit, but it excites one of the external electrons of the atom by photoelectric effect → Auger electron spectroscopy

Molecules/I.

H_2^+, bonding and anti-bonding molecular orbitals

V5

Question: Why are the molecules such as they are?

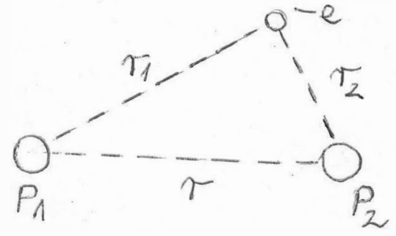
What is a molecule?

- group of nuclei surrounded by electrons in a stable arrangement?
- individual atoms held together by some interaction?

H_2^+ Hydrogen molecule ion

$2p + 1e \qquad H + H^+ = H_2^+$

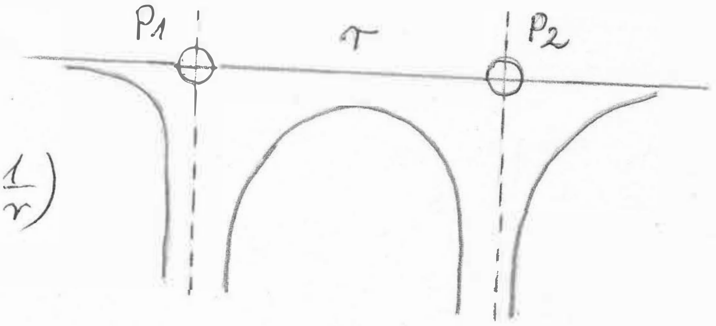
The electron does not "know" which proton it belongs to



Stationary states:

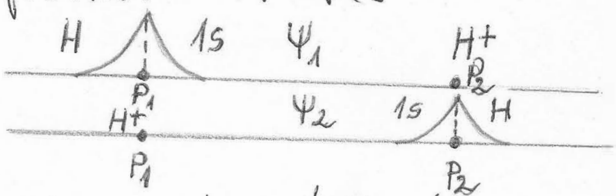
Schrödinger equation

Potential $E_p = \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r}\right)$



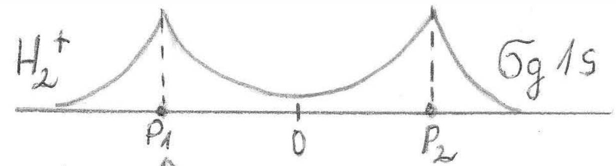
The wavefunction

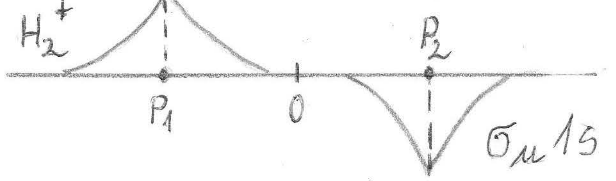
- 2 protons far away, 2 possible states
  - el. around p_1: 1s H atom, p_2 far
  - el. around p_2: 1s H atom, p_1 far



- Approaching the 2 protons: the free proton tries to pull the electron
- 2 protons close by

  Ψ_{el} must follow the symetry of the potential



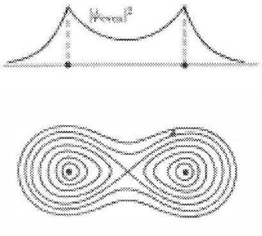


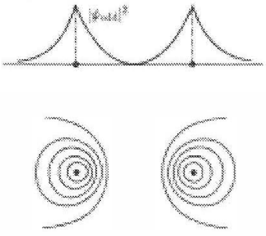
$\psi_{even} \approx \psi_1 + \psi_2 = \sigma_g 1s$

$\psi_{odd} \approx \psi_1 - \psi_2 = \sigma_u 1s$

Generation of molecular orbitals by linear combination of atomic orbitals

The probability distibution $|\psi|^2$





The energy of the two states are different, because

Electron between 2p – helps to pull the 2p together against the repellent Coulomb force

Electron outside 2p – they further pull the 2p away

$\rightsquigarrow \sigma_g 1s$ has lower energy

Approaching 2p:

- $\sigma_g 1s$ energy decreases until r_0, increases closer due to Coulomb repellence
- $\sigma_u 1s$ increases all the way

$r = r_0 \mapsto$ minimum in potential energy for $\sigma_g 1s$

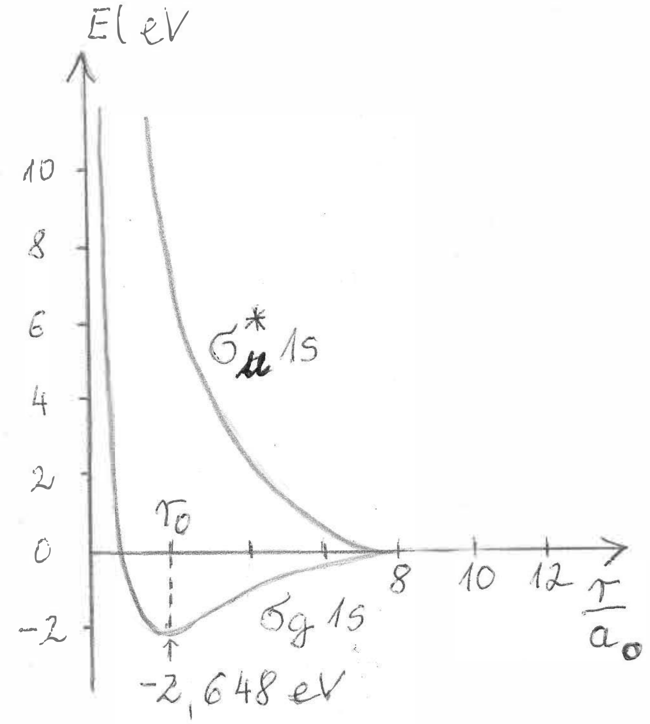
$\Downarrow$

Stable H_2^+ configuration

$\rightsquigarrow \sigma_g 1s$ bonding wavefunction

$\sigma_u 1s$ antibonding wavefunction (no energy minimum)

Denotion $\sigma_u 1s^*$



$r_0 = 1{,}06$ Å

The energy of these states!

$E = \int \psi^* \hat{H} \psi \, d\tau$ $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r}\right)$

The result is

$$E = E_a + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{A \pm B}{1 \pm S}$$

$\psi = \psi_g$ even

$\psi = \psi_u$ odd

Let ψ_1 and ψ_2 atomic wavefunctions belonging to the same E_a energy. (ψ are linear combinations of ψ_1 and ψ_2)

$\frac{e^2}{4\pi\varepsilon_0 r}$ → repellent potential of the 2 protons

$$A = \frac{e^2}{4\pi\varepsilon_0}\int \frac{\psi_1^2}{r_2}\, d\tau = \frac{e^2}{4\pi\varepsilon_0}\int \frac{\psi_2^2}{r_1}\, d\tau$$

This is the attractive potential between the electron near to one of the protons and the other proton

$$B = \frac{e^2}{4\pi\varepsilon_0}\int \frac{\psi_1 \psi_2}{r_1}\, d\tau = \frac{e^2}{4\pi\varepsilon_0}\int \frac{\psi_1 \psi_2}{r_2}\, d\tau$$

$$S = \int \psi_1 \psi_2 \, d\tau$$

B and S are quantum-mechanical terms

B and S are related to the overlap of the atomic wavefunctions

No overlap $B = S = 0$

$$E = E_a + \frac{e^2}{4\pi\varepsilon_0 r} - A$$

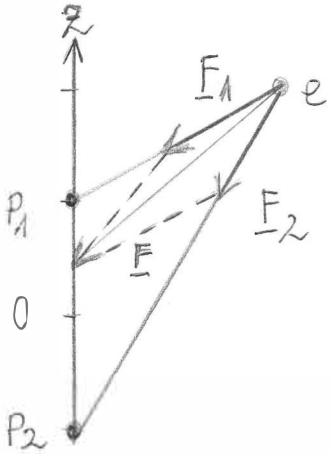
— no minima

The stable molecule can be explained with the overlap of the wavefunctions and the symmetry of the wavefunction.

Molecular orbital of diatomic molecules

H_2 → 2 electrons

Exclusion principle P: spin plays a role beside orbitals



the force is not centrally but axially symmetric

⇝ $\underline{L}$ is not constant of motion

Since the force $\underline{F}$ always intersects with the z axes, the torque on the electron is ⊥ to the axes ⇝ L_z = constant

$L_z = m_\ell \hbar \quad m_\ell = 0, \pm 1, \pm 2 \ldots$

The energy depends on $|m_\ell| = \lambda$ only (direction of rotation does not play a role)

The states

m_ℓ	0	± 1	± 2	$\pm 3 \ldots$	
λ	0	1	2	3	
denotion	σ	π	δ	φ	
number of states	2	4	4	4	$m_s = \pm \frac{1}{2}$

Denotion of molecular orbitals: $\lambda n \ell$

$\lambda = \sigma, \pi, \delta \ldots$

n, ℓ quantum numbers of the atomic orbitals which are combined for the molecular orbital

Homonuclear molecules: identical atoms

e.g. H_2

Potential symmetric to center ⤳

ψ is symmetric too

Two kinds of ψ: even and odd (g, u)

σ_g, σ_u, π_g, π_u etc.

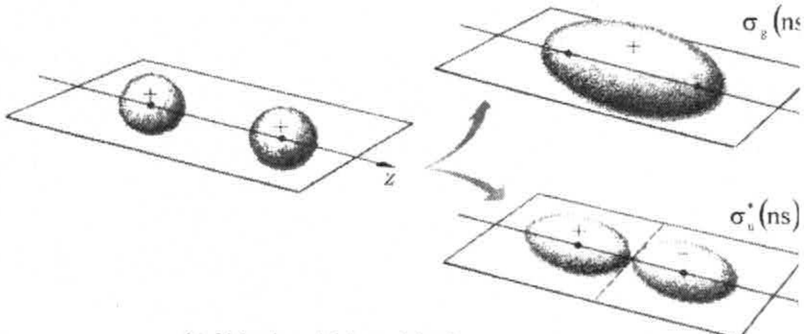
Chemical bond: approaching two atoms

$\psi_1 \pm \psi_2$

Angular distributions:

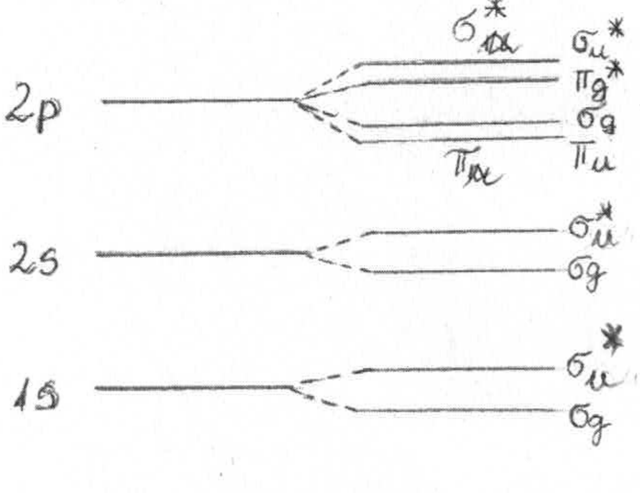
nodal planes - - -

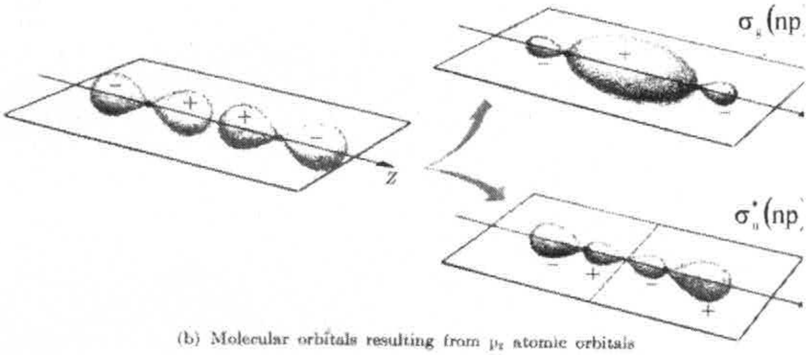
antibonding states (*)



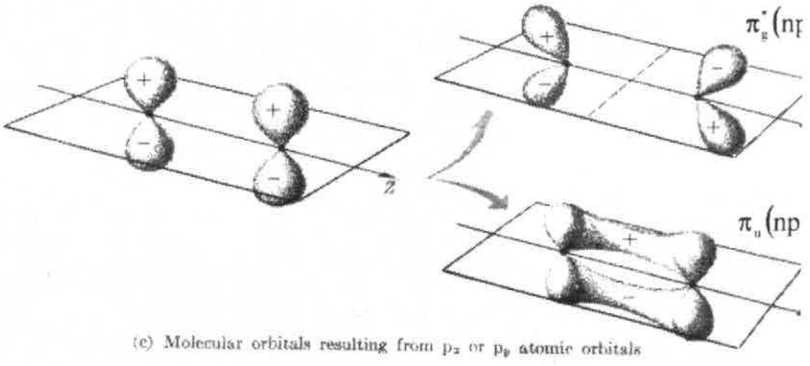
(a) Molecular orbitals resulting from s atomic orbitals

The energy levels of individual states





(b) Molecular orbitals resulting from p_z atomic orbitals

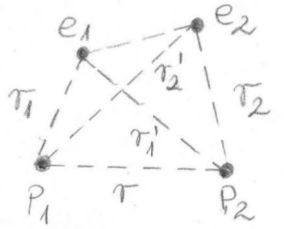


(c) Molecular orbitals resulting from p_x or p_y atomic orbitals

The actual energy levels, and energy differences depend on the particular molecule

Molecules/2.

Homonuclear molecules



$H_2 \to 2p + 2e$

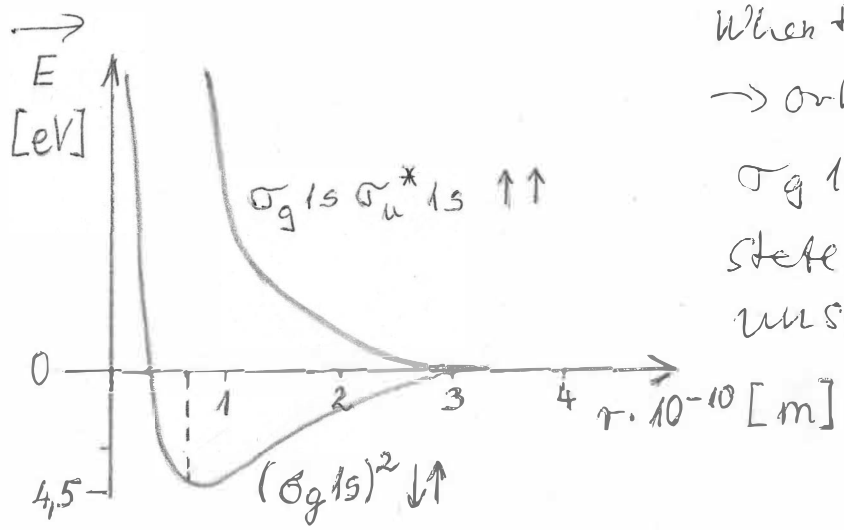
$$E_p = \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_1} - \frac{1}{r_1'} - \frac{1}{r_2} - \frac{1}{r_2'} + \frac{1}{r_{12}} + \frac{1}{r}\right)$$

One can not tell which electron belongs to which proton

Exclusion principle ; spin must be taken into account

→ 2 electrons on $\sigma_g 1s$ bonding state → ↑↓ spins

$(\sigma_g 1s)^2$ configuration → stable molecule



When the two spins are ↑↑
→ orbital must be antisymmetric
$\sigma_g 1s\, \sigma_u^* 1s$ → the antibonding
state dominates
unstable

He_2^+ molecule

3 electrons

$(\sigma_g 1s)^2 \sigma_u^* 1s$ configuration : stable

Total orbital angular momentum $M_L \hbar$

$M_L = \sum_i m_{li}$

The energy depends on $\Lambda = |M_L|$

$\Lambda = 0, 1, 2, \ldots$ $\Sigma, \Pi, \Delta, \Phi \ldots$ states

$^{2S+1}\Lambda$ S = total spin

Electron configuration of homonuclear diatomic molecules

	$\sigma_g 1s$	$\sigma_u^* 1s$	$\sigma_g 2s$	$\sigma_u^* 2s$	$\pi_u 2p$	$\sigma_g 2p$	$\pi_g^* 2p$	$\sigma_u^* 2p$	
H_2^+	↑								2,65
H_2	↑↓								4,48
He_2^+	↑↓	↑							3,1
He_2	↑↓	↑↓							instab.
Li_2	↑↓	↑↓	↑↓						1,03
Be_2	↑↓	↑↓	↑↓	↑↓					instab.
B_2	↑↓	↑↓	↑↓	↑↓	↑↑..				3,6
C_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓				3,6
N_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓			7,37
O_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑..		5,08
F_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑↓↓		2,8
Ne_2	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑↓↓	↑↓	instab.

The orbitals are filled sequentially with increasing energy

- Molecular bond: when electrons with opposite spin stay with high probability between the nuclei bonding states → covalent bond
- Exceptions: B_2, O_2 ↑↑ spins! Reason: π orbitals but only 2 electrons (instead of 4), due to repellence the antisymmetric orbital is energetically optimal ⇝ spins ↑↑ → permanent magnetic moment ⇒ paramagnetic
- He_2, Be_2: equal no. of bonding and antibonding orbitals → they are unstable
- N_2, O_2, F_2, Ne_2: dissociation energy (stability) decreases monotoniously because the difference in the number of bonding and antibonding pairs is 3, 2, 1, 0

Heteronuclear molecules

e.g. HCl, CO, NaCl ...

No centre of symmetry!

Orbitals: σ, π, δ but no g and u combinations

Electrons on the unfilled shells participate in the bond only

– E.g. NaCl Na: 11e, Cl: 17e but
outside the closed shells, the number of uncompensated spin electrons: Na 1el. 3s Cl 1el 3p

The nuclear charges are different $Z_{Na} = 11$, $Z_{Cl} = 17$

~> the negative charge shifts toward the Cl

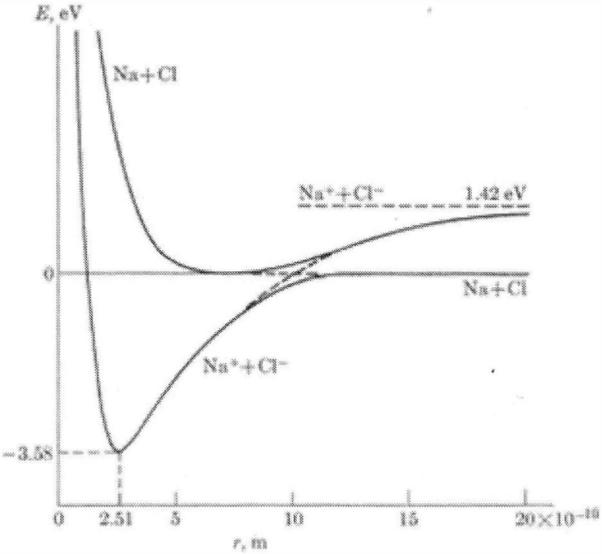
polarization → electric dipole moment: $3 \cdot 10^{-29}$ Cm

If the electron of Na was shifted completely to the position of Cl $e = 1{,}6 \cdot 10^{-19}$ C $d = 2{,}5 \cdot 10^{-10}$ m $e \cdot d = 4 \cdot 10^{-29}$ Cm

~ The electron of Na can be found with 75% probability at the position of Cl

⇒ They can be considered ions Na^+, Cl^-

Electric attraction ⟼ ionic bond



The wavefunction
$\varphi = \psi_A + \lambda \psi_b$
ψ_A and ψ_B atomic wavefunctions,
λ → from experiments

Most heteronuclear molecules' bond is between covalent and ionic bond

e.g. CO – more covalent than ionic $e \cdot d = 4 \cdot 10^{-31}$ Cm

(63)

Multiatomic molecules

Interesting: geometrical arrangement (symmetry)

Principle: the chemical bond between two atoms is formed in the direction where overlap of the atomic wavefunctions is maximum

E.g. H_2O

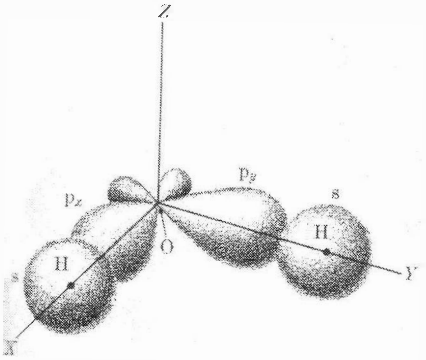
oxygen

	s	p		
L	↑↓	↑↓	↑	↑
K	↑↓			

2 electrons ↑↑ spins must have different orbitals: px, py

the two hydrogens: 1s electrons

Maximal overlap



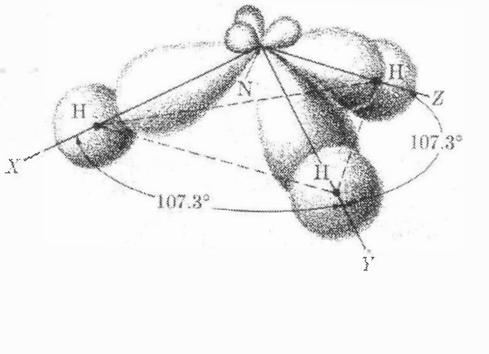
The p orbitals of the el-s of oxygen are distorted because of the H atoms
→ dipole moment
Angle > 90° (= 104,5°), because H atoms repel each other

NH_3

nitrogen

	s	p		
L	↑↓	↑	↑	↑
K	↑↓			

3 uncompensated spin p electron
px, py, pz
3 Hs : 1s electrons



Angle > 90° (107,3°) because the H atoms repel each other
pyramidal shape
distorted charge distribution
→ dipole moment (pyramid axes)

Hydrocarbon molecules

Valence of carbon is 4

ground state C

s	p		
↑↓	↑	↑	
↑↓			

excited state C*

s	p		
↑	↑	↑	↑
↑↓			

But: the s and p electrons are not equivalent from directionality point of view

CH4 ?

Hybridization

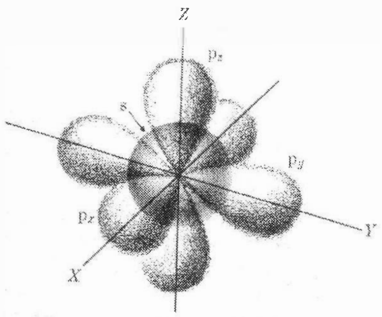
4 equivalent wavefunctions from linear combination of s, px, py, and pz → sp³ hybridization

$$\Psi_1 = \frac{1}{2}(s + p_x + p_y + p_z)$$

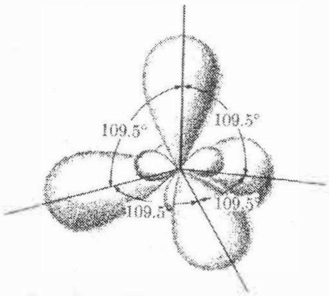
$$\Psi_2 = \frac{1}{2}(s + p_x - p_y - p_z)$$

$$\Psi_3 = \frac{1}{2}(s - p_x + p_y - p_z)$$

$$\Psi_4 = \frac{1}{2}(s - p_x - p_y + p_z)$$



(a) s, px, py, and pz wave functions

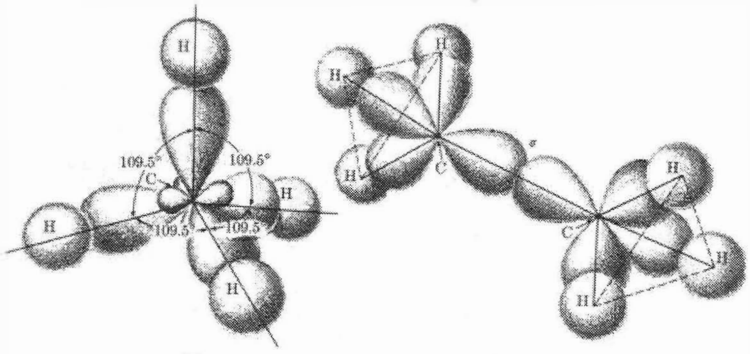


(b) sp³ hybridized wave functions

ψ_i → not eigenfunctions of angular momentum.

sp³ hybridization describes

CH4 methane   C2H6 ethane



(a)   (b)

Ethane $H_3C - CH_3$

↓

C – C bond with overlap of two sp³ hybrids: σ bond

Hybridization occurs at other orbitals (and other atoms) as well. Reason: energetically favorable.

sp² hybridization

s, px, py hybridizes + pz

$$\left.\begin{aligned}\psi_1 &= \frac{1}{\sqrt{3}}\left(s+\sqrt{2}\,p_x\right)\\ \psi_2 &= \frac{1}{\sqrt{3}}\left(s-\frac{1}{\sqrt{2}}p_x+\sqrt{\frac{3}{2}}\,p_y\right)\\ \psi_3 &= \frac{1}{\sqrt{3}}\left(s-\frac{1}{\sqrt{2}}p_x-\sqrt{\frac{3}{2}}\,p_y\right)\end{aligned}\right\}$$

In the x, y plane at 120°

$$\psi_4 = p_z$$

Ethylene : C_2H_4

$$H_2C \underset{\uparrow}{=} CH_2$$

σ π bond

σ between two sp² -s

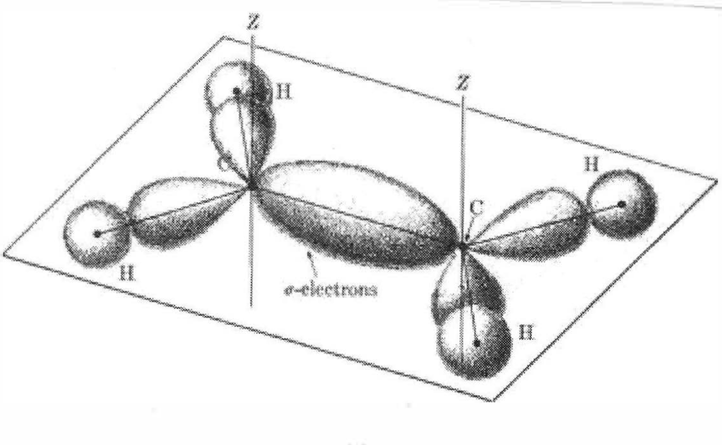
π between two pz -s

π : weaker than σ

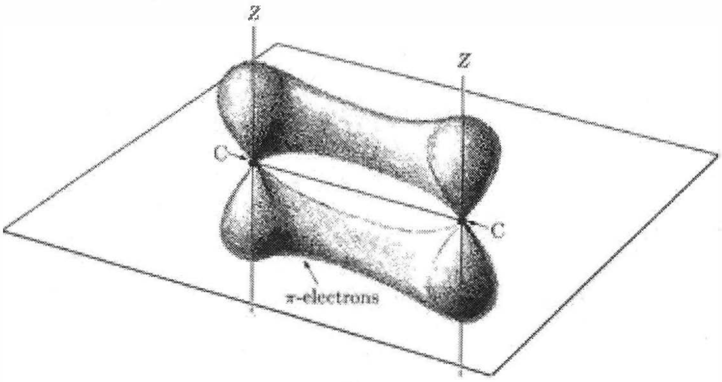
σ π bond : stiff

can not be rotated

around the C=C axes



(a)



(b)

sp hybridization

$$\psi_1 = p_x$$

$$\psi_2 = p_y$$

$$\left.\begin{aligned}\psi_3 &= s + p_z\\ \psi_4 &= s - p_z\end{aligned}\right\}\ \text{sp hybrids}$$

Acetylene : C_2H_2

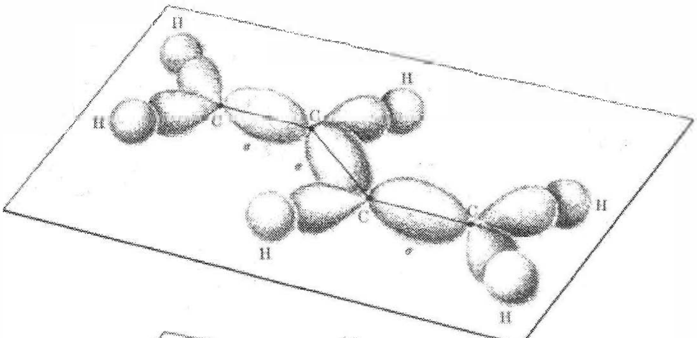
$$HC \underset{\uparrow}{\equiv} CH$$

σ 2π bond

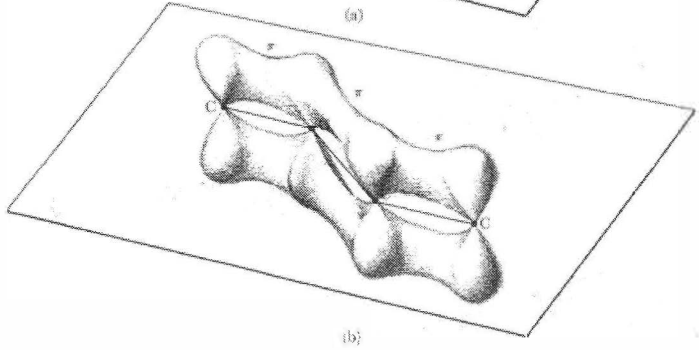
σ between two sp hybrids

π between px -s and
py -s

Conjugated molecules   e.g. C_4H_6 butadiene



(a)



(b)

sp^2 hybridization

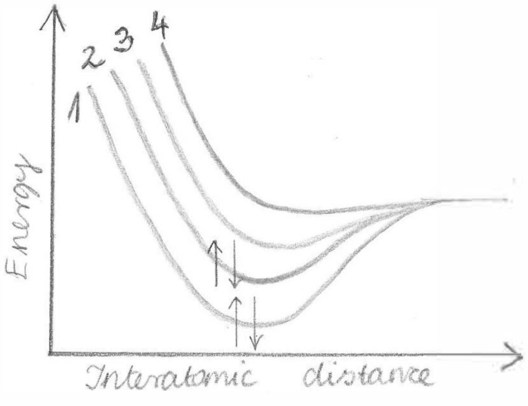
C atoms with σ bonds along the chain

H-C with sp^2

There remain 4 p_z electrons → π bond along the chain

These electrons are not localized, they move freely along the chain

Their wavefunctions: with combination of atomic orbitals



4 wavefunctions
4 energy levels
but only 2 are filled,
2 are empty ⇝
absorption in the visible
↓
colour

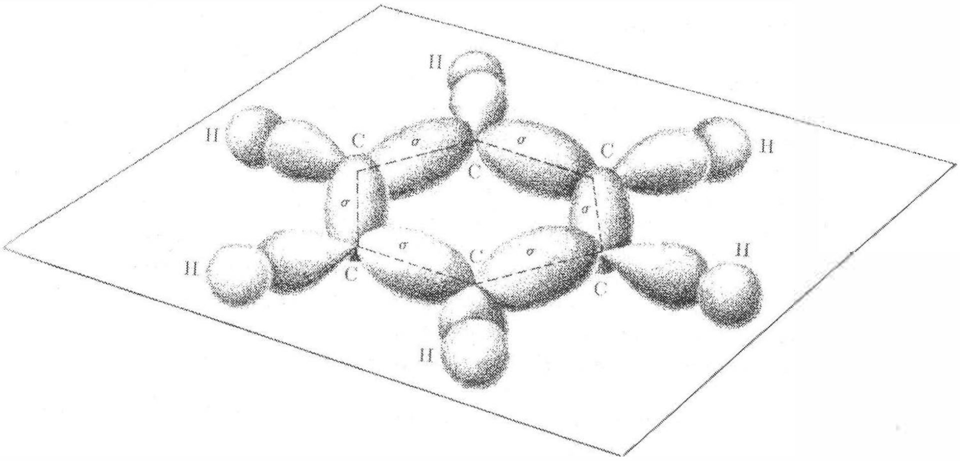
Polyene chain molecules consist of 2n C atoms are similar

$\ldots - C = C - C = C - C = \ldots$

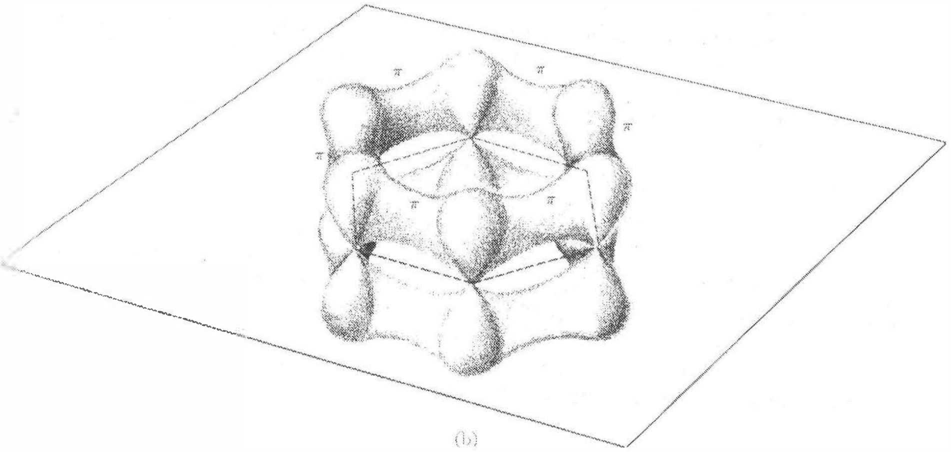
2 nπ electrons, 2n energy levels with 4n electron states.

Cyclic conjugated molecules

e.g. benzene C_6H_6 sp^2 hybridization



(a)



(b)

6π electrons move freely

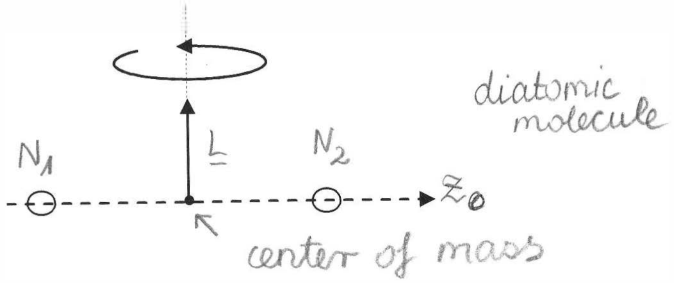
closed current loop → diamagnetic

(Lenz's law)

Rotation and vibration of molecules

Motion of atoms of the molecules in space and relative to each other

Rotation



r_0 distance in equilibr.

μ reduced mass

Moment of inertia $I = \mu r_0^2$

$\underline{L}$ angular momentum

Rotational energy: $E_r = \frac{L^2}{2I}$

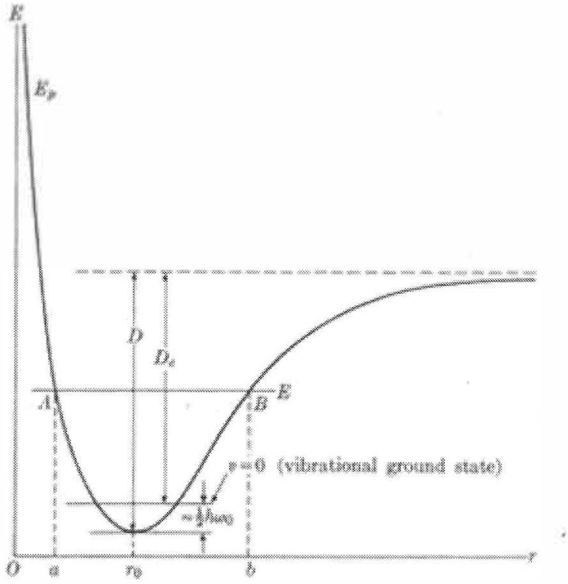
Quantization $L^2 = \hbar^2 \, l(l+1)$

$E_r = \frac{\hbar^2}{2I} l(l+1)$ $\quad \frac{\hbar^2}{2I} \sim 10^{-4}$ eV small → excited at room temperature

Selection rules: $\Delta l = \pm 1$

$\nu = \frac{\Delta E}{h} = \frac{\hbar}{2\pi I} \cdot l$ → equidistant spectral lines

Vibration



← the potential energy between a and b harmonic oscillator pot.

$E_v = \left(v + \frac{1}{2}\right)\hbar\omega_0$

Selection rule: $\Delta v = \pm 1$

$\hbar\omega_0 \sim 0{,}1 - 0{,}5$ eV infrared

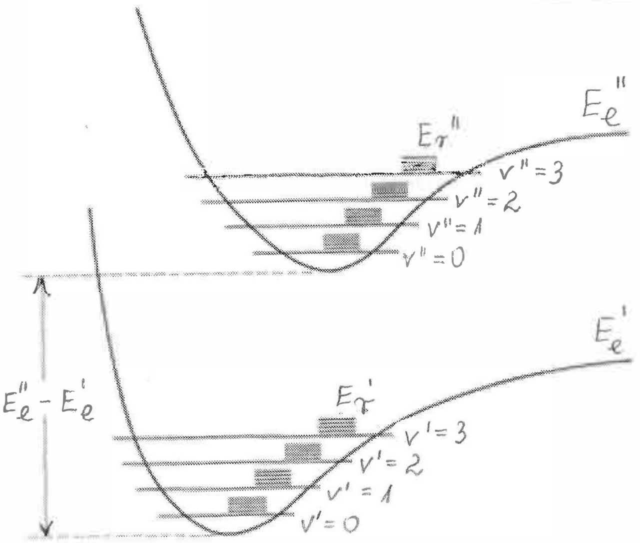
(D = dissociation energy)

The full energy:

$$E = E_e + E_v + E_r = \left(v + \frac{1}{2}\right)\hbar\omega_0 + \frac{\hbar^2}{2I} l(l+1) + E_e$$

E_e → energy of the electron state

$E = E_e + E_v + E_r$



Transitions

Bands in the electronic transitions

Selection rules

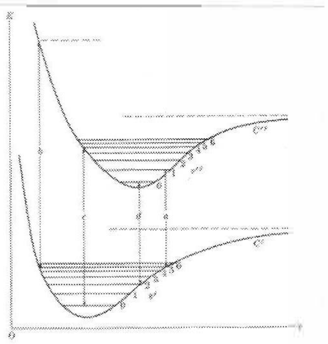
$\Delta L = 0, \pm 1$

$\Delta S = 0$

Vibrational selection rule ↓ when simultaneous electronic and vibrational transition

Time of the electronic transition $\sim 10^{-16}$ sec, while the vibr. period $\sim 10^{-13}$ sec (slow) ⇝

Franck-Condon principle : the transition is most probable, when the vibrational oscillation is at one of its extremes, and the interatomic distance of the initial and final states are equal.

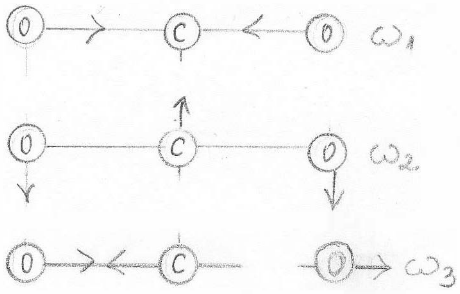


Vibration of multiatomic molecules

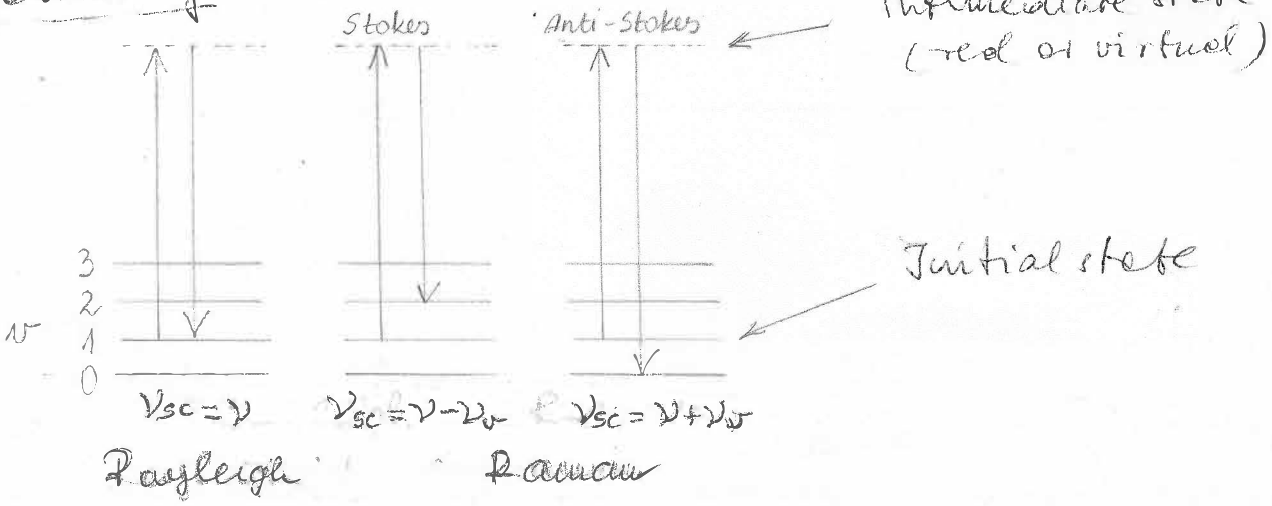
Normal modes (i) e.g. CO_2

combinations $\{v_i\}$

$E_v = \sum_i (v_i + \frac{1}{2}) \hbar \omega_i$



Rayleigh and Raman scattering



Statistical physics

Classical stat. phys.
Maxwell - Boltzmann distribution

System of large number of particles
e.g. $1 cm^3$ gas in normal state $\sim 3 \cdot 10^{19}$ molecules
Description of motion of each particle ↓
Purpose: description of possible states of the system
and their respective probabilities

Statistical equilibrium

N particles $E_1, E_2 \dots$ possible energy states of particles (continuous or discreet)

In E_i state n_i particles

$$N = \sum_i n_i$$

$$U = \sum_i n_i E_i$$ full energy of the system

Assumption: interaction of the particles can be taken into account with an average potential $E_i \rightarrow E_i + E_{i\,ave}$ $(= E_i)$

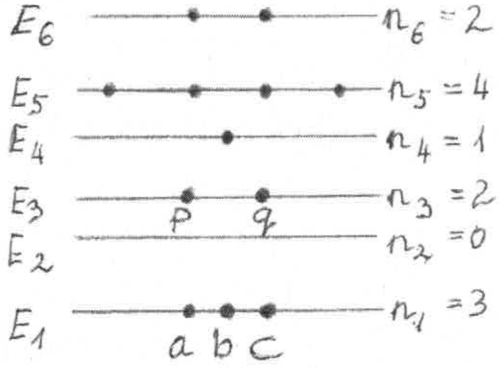
Closed system: $U = \text{const}$, but
due to the interaction (e.g. collision) of particles
the individual particles change their states $\rightsquigarrow$
$\{n_1, n_2, \dots\} = \{n_i\}$ distribution changes
$\exists$ a distribution with highest probability
$\{n_i\}_p$ = corresponds to the statistical equilibrium
We search for $\{n_i\}_p$ → macroscopic quantities can be derived from it

n_i fluctuates around $\{n_i\}_p$ but this has no macroscopically observable effect.

Maxwell - Boltzmann distribution (chemical particles)

System of identical and indistinguishable particles

First: assume distinguishability



Assumptions:

Possibility
1. Probability of filling ∀ energy state is identical $= \{n_1, n_2, n_3 \ldots\}$
2. Probability of an $\{n_i\}$ distribution is proportional to the number of its realication possibilities

→ ("a" at E_1 "p" at E_3 is different from "a" at E_3 and "p" at E_1 due to distinguishability of the particles)

No. of realisations:
From the N particles we can select n_1 particles to the E_1 state:

$\binom{N}{n_1} = \frac{N!}{n_1!(N-n_1)!}$ ways (number of combinations) binomial coefficient N choose n_1

After this we can select n_2 particles from $(N-n_1)$ to the E_2 sta

$\binom{N-n_1}{n_2}$ ways

So for $\forall\{E_i\}$ an $\{n_i\}$ configuration can be selected in

$$P \approx \frac{N!}{n_1!(N-n_1)!} \cdot \frac{(N-n_1)!}{n_2!(N-n_1-n_2)!} \cdot \ldots = \frac{N!}{n_1!n_2!n_3!\ldots}$$

ways.

According to 2. $P \approx$ probability of the $\{n_i\}$ distributi

When asumpt. 1. ∀ i possibility probability of getting to E_i is g_i

($g_i \equiv$ degree of degeneracy of E_i)

$$P \approx \frac{N!\, g_1^{n_1} g_2^{n_2} g_3^{n_3}}{n_1!\, n_2! \ldots} = N! \prod_i \frac{g_i^{n_i}}{n_i!}$$

no. of realisations

— Now when the particles are indistinguishable

⇝ N! permutation gives the same distribution

$$P \approx \frac{g_1^{n_1} g_2^{n_2} \ldots}{n_1!\, n_2! \ldots} = \prod_i \frac{g_i^{n_i}}{n_i!}$$

$$P = \prod_{i=1}^{N} \frac{g_i^{n_i}}{n_i}$$

$$P_{max} \equiv \ln P_{max}$$

$$\ln P = n_1 \ln g_1 + n_2 \ln \;\ldots - \ln n_1! - \ln n_2! \ldots$$

Stislings' form $\ln x! = x \ln x - x$ when x is large

$$\ln P = n_1 \ln g_1 + \ln g_2 + \ldots - (n_1 \ln n_1 - n_1) - (n_2 \ln n_2 - n_2) - \ldots =$$

$$= -n_1 \ln \frac{n_1}{g_1} - n_1 \ln \frac{n_2}{g_2} - \ldots + (n_1 + n_2 + \cdots)$$

$$= N - \sum_i n_i \ln \frac{n_i}{g_i}$$

Differentiating

$$d(\ln P) = -\sum_i dn_i \ln \frac{n_i}{g_i} - \sum_i n_i \, d \ln \frac{n_i}{g_i} =$$

$$\searrow \frac{d\left(\frac{n_i}{g_i}\right)}{\frac{n_i}{g_i}} \swarrow$$

$g_i = \text{const.}$

$$= \quad \downarrow \qquad -\sum_i \boxed{\cancel{n_i} \frac{dn_i}{\cancel{n_i}}} =$$

$$-d \ln P = \sum_i \left(\ln \frac{n_i}{g_i}\right) dn_i \qquad = \sum_i dn_i = 0 \;\; (U = \text{const.})$$

In the thermal equilibrium

$$P_{max} \rightarrow dP = 0 \rightarrow d \ln P = \frac{dP}{P} = 0$$

$$\sum_i \left(\ln \frac{n_i}{g_i}\right) dn_i = 0$$

Two conditions: $\sum_i dn_i = 0$

$\downarrow$ $\qquad \sum_i E_i dn_i = 0 \quad (U = \text{const})$

Tour-Lagrange undetermined multipliers α, β

$$\sum_i \left(\ln \frac{n_i}{g_i} + \alpha + \beta E_i\right) dn_i = 0 \qquad \ln \frac{n_i}{g_i} + \alpha + \beta E_i = 0$$

$$n_i = g_i e^{-\alpha - \beta E_i}$$

The most probable distribution (stat. equilibr.)

P_{max} $(dP=0)$ additional conditions: $\sum_i dn_i = 0$

(U and N are constant) $\sum_i E_i dn_i = 0$

$n_i = g_i e^{-\alpha - \beta E_i}$ $N = \sum_i n_i = e^{-\alpha} \underbrace{\sum_i g_i e^{-\beta E_i}}_{Z}$

Def.: partition function $Z = \sum_i g_i e^{-\beta E_i}$

$e^{-\alpha} = \frac{N}{Z} \rightsquigarrow \underline{n_i = \frac{N}{Z} g_i e^{-\beta E_i}}$ Maxwell-Boltzmann distribution

Average of energy dependent physical quantities

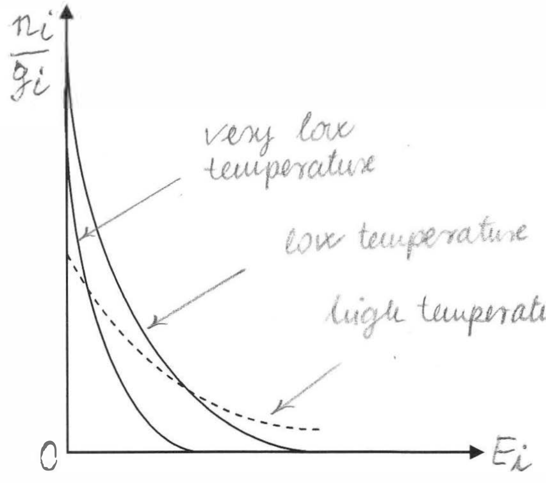
$$F_{ave} = \frac{1}{N}\sum_i n_i F(E_i) \overset{\text{in stat. equil.}}{=} \frac{1}{Z}\sum_i g_i F(E_i) e^{-\beta E_i}$$

What is β?

Def. $\beta = \frac{1}{kT}$ $k = 1{,}38 \cdot 10^{-23}$ J/°K Boltzmann constant

T = temperature (°K)

$$\left| \begin{array}{l} Z = \sum_i g_i e^{-\frac{E_i}{kT}} \\ n_i = \frac{N}{Z} g_i e^{-\frac{E_i}{kT}} \end{array} \right. \longrightarrow$$



The total energy is

$$U = \frac{N}{Z}\sum_i g_i E_i e^{-\beta E_i} =$$

$$= \frac{N}{Z}\frac{d}{d\beta}\left(\sum_i g_i e^{-\beta E_i}\right) =$$

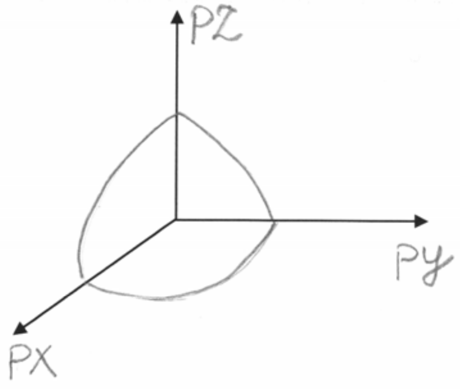
$$= -\frac{N}{Z}\frac{dZ}{d\beta} = -N\frac{d}{d\beta}(\ln Z)$$ but $d\beta = -\frac{dT}{kT^2} \rightsquigarrow$

$$U = kNT^2 \frac{d}{dT}(\ln Z).$$

Average energy of a particle $E_{ave} = kT^2 \frac{d}{dT}\ln Z$

$\rightsquigarrow$ the temperature of the system in statistical equilibrium depends on the average energy of the particles and on the structure of the system (Z)

$$E = \frac{p^2}{2m} \qquad p = (2mE)^{1/2}$$



$$N(E) = \frac{1}{8}\left(\frac{4\pi}{3} p_{max}^3\right) = \frac{1}{8}\frac{4\pi}{3} \cdot (2mE)^{3/2}$$

$$g(E) = \frac{dN(E)}{dE} = \frac{\pi}{\sqrt{2}} m^{3/2} E^{1/2} \qquad Z = \int g(E) e^{-\frac{E}{kT}} dE$$

$$Z = \int_0^\infty g(E) e^{-E/kT} dE = \frac{1}{2}\left(\frac{\pi}{2} mkT\right)^{3/2}$$

$$\int_0^\infty x e^{-\alpha x^2} dx = \frac{1}{2\alpha} \qquad x = E^{1/2}$$

$$E_{ave} = \frac{U}{N} = kT^2 \frac{d}{dT} \ln Z = \frac{3}{2} kT$$

$$\downarrow$$

$$\Big(kT^2 \frac{d}{dT} \ln Z = kT^2 \frac{d}{dT} \ln\left\{\frac{1}{2}\left(\frac{\pi}{2} mkT\right)^{3/2}\right\} =$$

$$= kT^2 \frac{d}{dT}\left\{\ln\frac{1}{2} + \frac{3}{2}\ln\frac{\pi}{2}mk + \frac{3}{2}\ln T\right\}$$

$$= kT^2 \frac{3}{2}\frac{1}{T} = \frac{3}{2} kT \Big)$$

E.g. population of the energy levels

$$\begin{array}{l} \text{———} E_j \\ \text{———} E_i \end{array} \updownarrow \Delta E \qquad \frac{n_j}{n_i} = \frac{g_j}{g_i} e^{-\frac{E_j - E_i}{kT}} = \frac{g_j}{g_i} e^{-\frac{\Delta E}{kT}}$$

Gas molecules in thermal equilibrium ; n_j / n_i

	ΔE [eV]	100 °K	300 °K	1000 °K
mol. rotational levels	10^{-4}	0,989	0,996	0,999
mol. vibration levels	$5 \cdot 10^{-2}$	$3 \cdot 10^{-3}$	$1{,}5 \cdot 10^{-1}$	$5{,}6 \cdot 10^{-1}$
electron excitation	3	$3 \cdot 10^{-164}$	$8 \cdot 10^{-49}$	$8 \cdot 10^{-16}$

E.g. ideal gas /one-atomic molecules, kinetic energy only/

$E_i = \frac{1}{2} m v_i^2$ not quantized $\quad Z = \int g(E)\, e^{-E/kT} dE$

$g(E)dE$ number of molecular states between E and $E + dE$
(different velocities $\underline{v}$)

We have seen at the potential box: $g(E) = \frac{4\pi V (2m^3)^{1/2}}{h^3} E^{1/2} \rightarrow$

$$Z = \frac{V(2\pi m k T)^{3/2}}{h^3} \rightsquigarrow \underline{E_{ave} = \frac{3}{2} kT} \;, \; U = N \cdot E_{ave} = \frac{3}{2} kTN$$

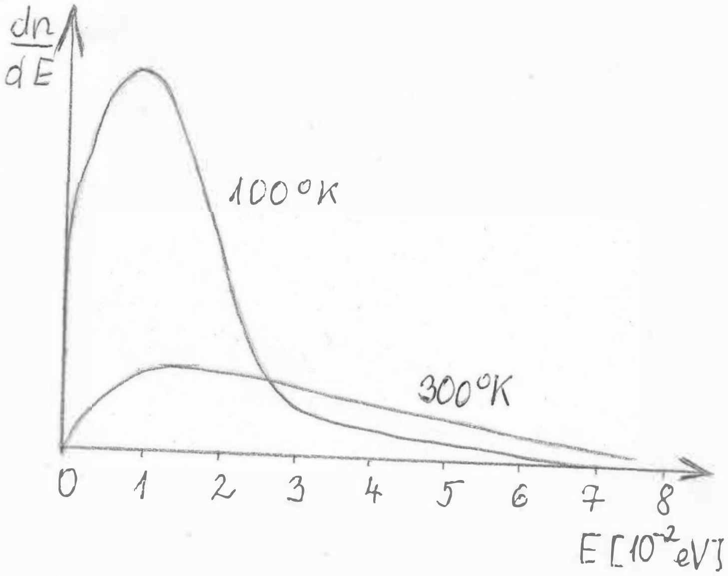
The distribution instead of n_i

$$dn = \frac{N}{Z} e^{-\frac{E}{kT}} g(E) dE$$

$$\frac{dn}{dE} = \frac{2\pi N}{(\pi k T)^{3/2}} E^{1/2} e^{-\frac{E}{kT}}$$

(independent of mass!)

Distribution by velocity



Maxwell - Boltzmann distribution: does not take into account limitations on the population of the E_i states. Restrictions of quantum mechanics

High temperatures and low densities:

∀ distribution - is equivalent with Maxwell - Boltzmann

Statistical physics II.

Quantum statistics
Fermi-Dirac & Bose-Einstein stat
Electromagnetic radiation

(E4)

Quantum statistics

Restrictions on the number of particles that can occupy the same state with any given energy.

⇝ Distribution function changes.

Particles: identical and indistinguishable

2 cases

1. Exclusion principle ✓ ⇝ antisymmetric wavefunction
   → Fermi-Dirac stat. fermions
2. Exclusion principle ✗ ⇝ symmetric wavefunction
   → Bose-Einstein stat. bosons

We look for the distribution of statistical equilibrium (most probable distr.)

1. Fermi-Dirac distribution

Particles with half spin (e.g. electrons)

$g_i \equiv$ the number of different quantum states with E_i energy $\equiv$ maximum number of fermions that can have E_i energy without violation of the exclusion principle, i.e.:

$$n_i \leq g_i$$

E.g. in a central force field $g_i = \sum_{l=0}^{n-1} 2(2l+1)$

→ When filling up the E_i states

1. particle g_i different states available
2. particle $g_i - 1$ — ″ — — ″ — — ″ —

For n_i particles there are

$$g_i(g_i-1)\cdots(g_i-n_i+1) = \frac{g_i!}{(g_i-n_i)!}$$

arrangements on the g_i states

But since the particles are indistinguishable the number of different distributions is

$$\frac{g_i!}{n_i!(g_i-n_i)!}$$

Number of realizations for ∀ levels:

$$P=\prod_i \frac{g_i!}{n_i!(g_i-n_i)!}$$ for an $\{n_i\}$ distribution

This is the probability of the $\{n_i\}$ distribution

Most probable distribution (stat. equilibr.) $\rightarrow P_{max}$

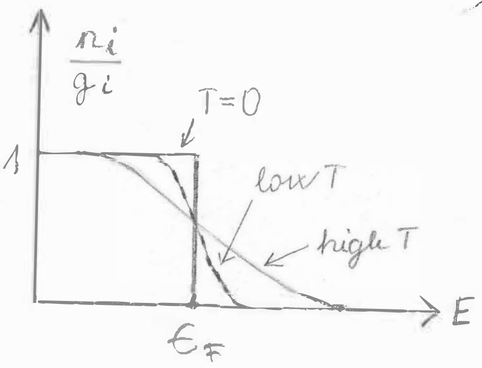
$$n_i = \frac{g_i}{e^{\alpha+\beta E_i}+1}$$ Fermi-Dirac distribution

$\beta = \frac{1}{kT}$ $\sum_i n_i = N \rightsquigarrow \alpha$

Def.: $\alpha = -\frac{\epsilon_F}{kT}$ ϵ_F = Fermi energy

(e.g. electrons in metals)

$$n_i = \frac{g_i}{e^{(E_i-\epsilon_F)/kT}+1}$$



T=0: Due to the exclusion principle ∀ atoms are not in ground state but fill up all the energy levels up to $E = \epsilon_F$ ($n_i = g_i$)

$E > \epsilon_F$ empty ($n_i = 0$)

$$\lim_{T\to 0} e^{\frac{(E_i-\epsilon_F)}{kT}} = \begin{cases} 0 & E_i-\epsilon_F<0 \\ 1 & E_i-\epsilon_F>0 \end{cases}$$

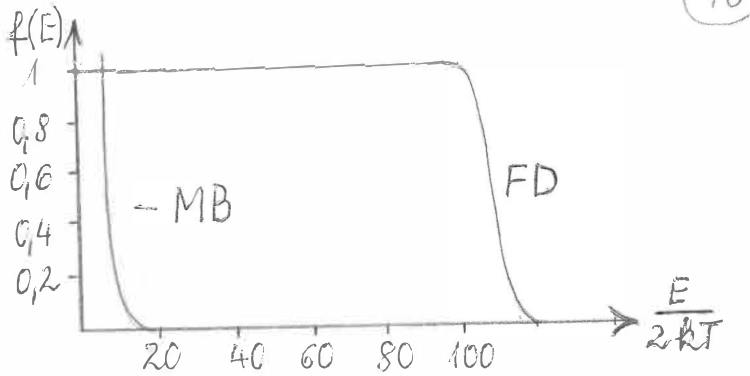
(For Maxw.-Boltzm. $T=0$ ∀ particles in ground state!)

$T>0$ but $kT \ll \epsilon_F \rightsquigarrow$ Population of states near to ϵ_F changes only, due to the exclusion principle

$\Theta_F = \epsilon_F/k$ – Fermi temperature

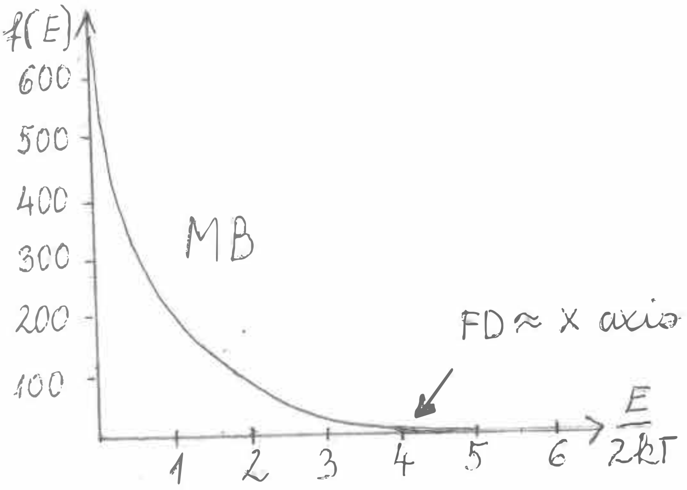
(electrons in metals $\Theta_F \approx 10^4$ °K)

Comparison of Maxwell-Boltzmann and Fermi-Dirac distribution at $T = 10^{-4} \Theta_F$



$$f(E) = \frac{n_i}{g_i}(E) = $$

$$= \frac{1}{e^{\frac{(E-\epsilon_F)}{kT}} + 1}$$



Total energy of N fermions at $T \approx 0$

$$U = \int E\, dN = \int E \frac{dn}{dE} dE = \int_0^{\epsilon_F} E \frac{dn}{dE} dE$$

$T = 0$ $\quad dn/dE = g(E) =$ density of states $= \frac{8\pi V(2m^3)^{1/2}}{h^3} \cdot E^{1/2}$

$$U = \frac{8\pi V(2m^3)^{1/2}}{h^3} \int_0^{\epsilon_F} E^{3/2} dE = \frac{16\pi V(2m^3)^{1/2}}{5h^3} \epsilon_F^{5/2}$$

For an ideal gas $U = \frac{3}{2} kNT$ $\quad T = 0 \rightsquigarrow U = 0\,/$

E.g. free electrons /conduction electrons/ in metals

No. of electrons between E and E + dE

$$dn = \frac{g(E)\, dE}{e^{(E-\epsilon_F)/kT} + 1} = \frac{8\pi V(2m^3)^{1/2}}{h^3} \frac{E^{1/2} dE}{e^{(E-\epsilon_F)/kT} + 1}$$

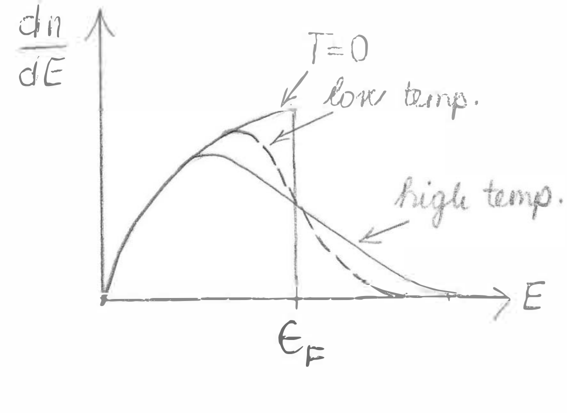
$$N = \int dn = \int_0^{\epsilon_F} \frac{dn}{dE} dE \rightsquigarrow$$

$$! \; \epsilon_F = \frac{h^2}{8m} \left(\frac{3N}{\pi V}\right)^{2/3} \leftarrow$$

Depends on the electron density

$$U = \frac{3}{5} N \cdot \epsilon_F$$

ϵ_F for metals tipically few eV



2. Bose-Einstein statistic

Identical and indistinguishable particles, for the system of which the exclusion principle ↓ $\rightsquigarrow$ there can be any number of particles in the same state

The wavefunction of the system is symmetric

Particles with integer spin (0, 1, ..) e.g. ^{4}He nucleus, H_2 ..

system of even number of half spin particles, Cooper pairs, photons

Let the degree of degeneracy of the E_i state be g_i
n_i particles can occupy these degenerate states in $(n_i+g_i-1)!$ ways when the particles are distinguishable. For indistinguishable particles permutations of n_i and g_i-1 give the same distribution $\rightsquigarrow$ the number of distinguishable distributions is

$$\frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}$$

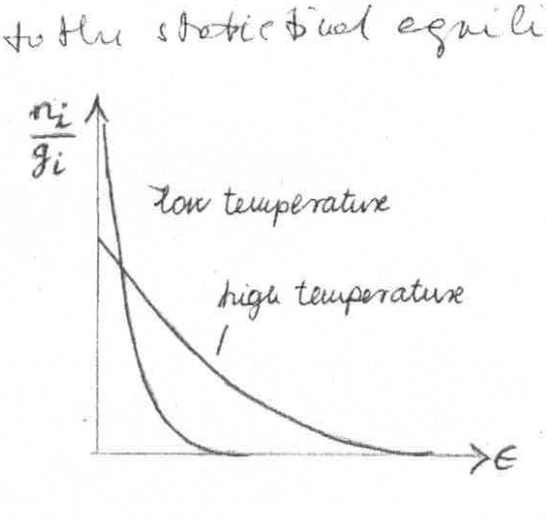
n_i particles
g_i states → $g_i - 1$ walls
with E_i energy

The probability of $\{n_i\}$ distr.

$$P \sim \prod_i \frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}$$

Its maximum corresponds to the statistical equilibrium

$$n_i = \frac{g_i}{e^{\alpha+\beta E_i}-1}$$



$\beta = \frac{1}{kT}$

$N = \sum_i n_i \rightsquigarrow \alpha$

$\alpha \geq 0$, because $n_i \geq 0$

Population of lower energy levels is higher than for the Maxw. Boltzm. distribution

The photon "gas"

Electromagnetic radiation in a cavity in thermal equilibrium with the walls of the cavity (dinamic equilibrium: absorption and emission rates of the wall are identical)

Search: energy distribution of the electromagnetic radiation (spectrum)

Electromagnetic radiation: in absorption and emission processes behaves like particles

photons
- emission processes behaves like particles
- Energy: $h\nu$, momentum h/λ, indistinguishable, with each other non-interacting particles
- Any number of particles with given energy → **bosons** / angular momentum = 1 (circ. pol.)

The particle number in the cavity ≠ const. since the walls can absorb or emit ~ α arbitrary in thermal equilibr. Let $\alpha = 0$

In statistical equilibrium

$$n_i = \frac{g_i}{e^{E_i/kT}-1}$$

Possible energy states continuous

$$g_i \to g(E)\,dE$$

$$dn = \frac{g(E)\,dE}{e^{E/kT}-1}$$ number of photons between E and $E+dE$

Density of states

$$g(E)\,dE = g(\nu)\,d\nu$$ since $E = h\nu$

In a cavity with volume V the numbers of states with E energy → density of states

$$g(E) = \frac{4\pi V(2m^3)^{1/2}}{h^3} E^{1/2}$$

$$p = \sqrt{2mE} = \frac{h}{\lambda} \qquad \nu = \frac{c}{\lambda}$$

$$g(\nu) = \frac{4\pi V}{c^3}\nu^2$$

Electromagnetic wave - transverse → 2 polarizations

$$g(E)dE = g(\nu)d\nu = \frac{8\pi V}{c^3}\nu^2 d\nu$$ with this

$$dn = \frac{8\pi V}{c^3}\frac{\nu^2 d\nu}{e^{h\nu/kT}-1}$$

Energy of a photon $h\nu$, volume of cavity is V

The energy density $E(\nu) = \frac{h\nu}{V}\frac{dn}{d\nu}$

$$\varepsilon(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{kT}}-1}$$ Planck's law for the blackbody radiation

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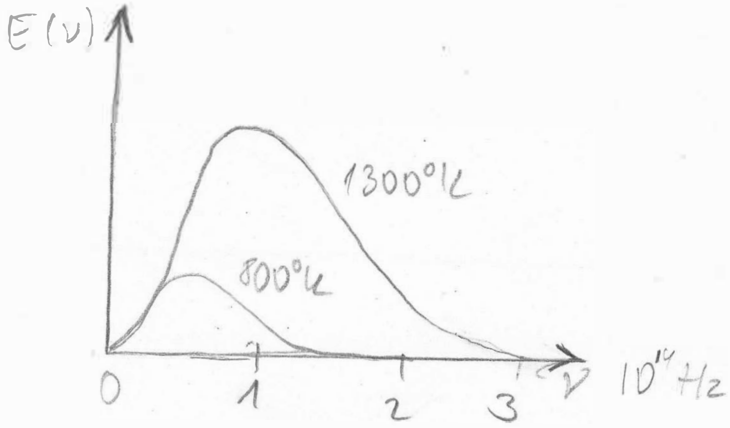
Considering the electromagnetic radiation as system of particles following Bose-Einstein statistics we get a spectrum corresponding to experimental results!



$g(\nu) = ?$ *

$$E = \frac{p^2}{2m} \qquad \cancel{\frac{dE}{dp} = \frac{p}{m}} \qquad \frac{dE}{dp} = \frac{p}{m}$$

$$g(E) = \frac{4\pi V (2m^3)^{1/2}}{h^3} E^{1/2} = \frac{4\pi V (2m^3)^{1/2}}{h^3} \frac{p}{\sqrt{2m}} = \frac{4\pi V}{h^3} \cancel{2} m \cdot p$$

$$\frac{dN}{dp} = g(p) = g(E)\frac{dE}{dp} = \frac{4\pi V}{h^3} \cancel{2} m \cdot p \cdot \frac{p}{m} = \frac{8\pi V}{h^3} p^2$$

$$p = \frac{h\nu}{c} \qquad dp = \frac{h}{c} d\nu$$

$$\frac{dN}{\frac{h}{c} d\nu} = \frac{8\pi V}{h^3} \frac{h^2 \nu^2}{c^2}$$

$$\frac{dN}{d\nu} = \frac{\cancel{h}}{c} \frac{8\pi V}{\cancel{h^3}} \frac{\cancel{h^2} \nu^2}{c^2} = \frac{8\pi V}{c^3} \nu^2$$

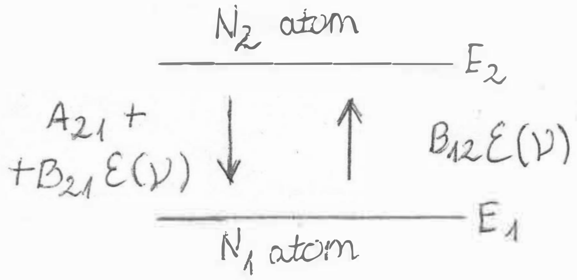
$$\shortparallel$$

$$g(\nu) = \frac{8\pi V}{c^3} \nu^2 \qquad \times 2$$

(2 independent polarization)

Interaction of light and matter

How does material (walls of the cavity or a gas in the cavity) interacting with e.m. radiation in thermal equilibrium?



Model: 2 states

$\Delta E = E_2 - E_1$

$h\nu = \Delta E$ transition between 2 states

$\varepsilon(\nu)$ = energy density

The absorption probability per unit time

$$B_{12}\,\varepsilon(\nu)$$

$B_{12} = W(1\to2)$ transition probability per unit time and unit energy density

Interaction with particles at level E_2

$B_{21}\,\varepsilon(\nu)$ induced emission probability
A_{21} spontaneous –"– –"–

In unit time

No. of $N_2 \to N_1$ transitions $[A_{21} + B_{21}\,\varepsilon(\nu)]N_2$

No. of $N_1 \to N_2$ transitions $B_{12}\,\varepsilon(\nu)N_1$

$$\frac{dN_2}{dt} = \underbrace{B_{12}\,\varepsilon(\nu)N_1}_{\text{absorption}} - \underbrace{[A_{21} + B_{21}\,\varepsilon(\nu)]N_2}_{\text{emission}}$$

In thermal equilibrium $dN_2/dt = 0$ and the atoms $N_1/N_2 = e^{(E_2-E_1)kT} = e^{h\nu/kT}$ Maxwell-Boltzmann distribution

$B_{12}\,\varepsilon(\nu)e^{h\nu/kT} = A_{21} + B_{21}\,\varepsilon(\nu) \rightsquigarrow$

$$\varepsilon(\nu) = \frac{A_{21} + B_{12}}{e^{h\nu/kT} - B_{21}/B_{12}}$$ ← Shape of spectrum ≡ ≡ Planck's law!

From Planck's law

$B_{12} = B_{21}$ $\quad A_{21} = \frac{8\pi\nu^3}{c^3} B_{21}$ ← probability of spontaneous emission

absorption prob. = ind. em. probability $(W(i \to k) = W(k \to i))$

$$\frac{\text{Spont. em. probab.}}{\text{Ind. em. probab.}} = \frac{A_{21}}{B_{21}\,\varepsilon(\nu)} = e^{\frac{h\nu}{kT}} - 1$$

$\frac{h\nu}{kT} \gg 1$ induced emission insignificant (electronic transitions fr. above light)

$\frac{h\nu}{kT} \ll 1$ induced emission is significant (e.g. microwaves)

Induced emission: photon generated with identical frequency and phase with the incident photon → coherent

Spontaneous emission: incoherent

Principle of laser operation

$$\frac{\text{Prob. emission/unit time}}{\text{Prob. absorption/unit time}} = \frac{\left[A_{21} + B_{21}(\varepsilon(\nu))\right] N_2}{B_{12}\,\varepsilon(\nu)\, N_1} =$$

$$= \left(1 + \frac{A_{21}}{B_{21}(\varepsilon(\nu))}\right)\frac{N_2}{N_1}$$

If the system of atoms is not in thermal equilibrium

$N_2 > N_1$ is possible ⇝ emission > absorption

The medium amplifies the e.m. radiation

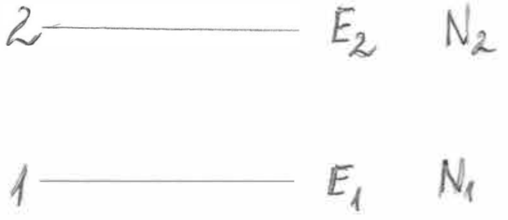
$N_2 > N_1$ inverse population ← with external pumping

Amplification — coherent

Amplifier + feedback ≡ oscillator

Feedback — optical resonator

Lasers



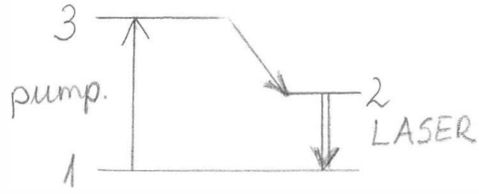
F = photon flux

$$dF = \sigma F\,(N_2 - N_1)\,dz$$

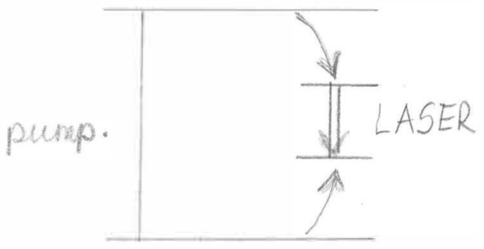
$$\frac{N_2}{N_1} = e^{-\frac{E_2-E_1}{kt}} < 1 \rightsquigarrow dF < 0$$

$$\frac{N_2}{N_1} > 1 \rightsquigarrow dF > 0\ !$$

Amplifier.

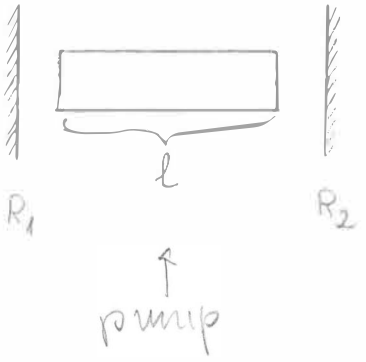


(impulse mode)



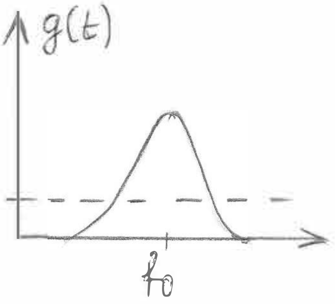
(continuous mode)

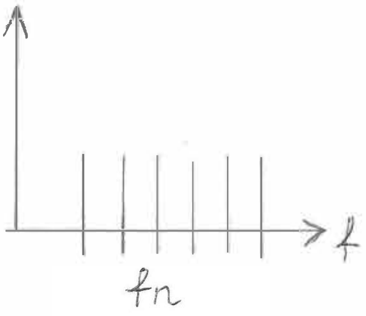
Oscillator.



$$e^{\sigma(N_2-N_1)\cdot l}\cdot R_1\cdot R_2 > 1$$

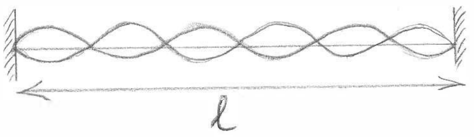
$$(N_2 - N_1) \geq \frac{\ln R_1 R_2}{\sigma l}$$

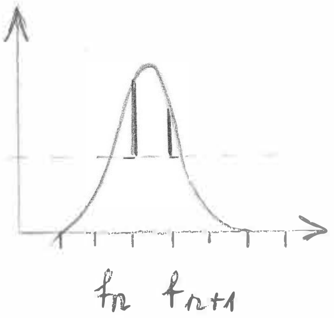




resonator modes

$$f_n = n \cdot \frac{c}{2l}$$





Gauss beams $I(r) \sim e^{-\frac{r^2}{w^2}}$

Gaslasers : He-Ne, CO_2 ...

solid : Nd:YAG, Nd: glass

semiconductor: AlGaAs, GaAsP...

Coherence