LASER PHYSICS

LASER PHYSICS
PHYSICAL FOUNDATIONS
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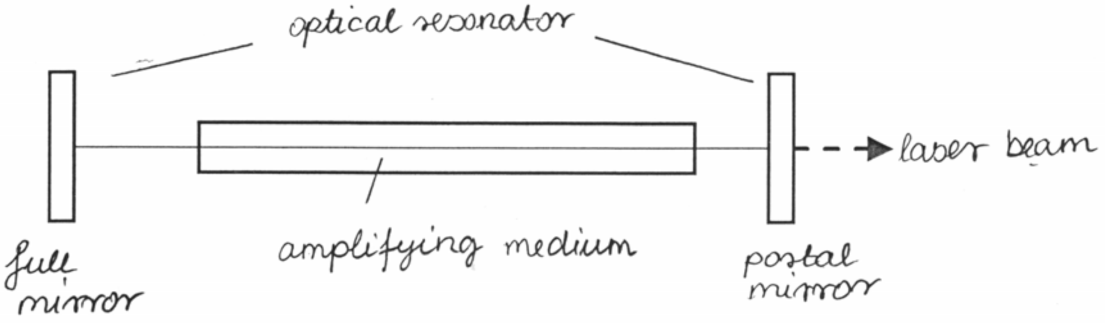
INTRODUCTION

LASER



Bright ! 1 mrad → 10^{-6} sr lightbulb 2π sr

Unique properties : parallel

monochromatic (e.g. He-Ne ~ 1 MHz
spectral Hg lamp 10^8 Hz
lightbulb $10^{12} - 10^{15}$ Hz

focusability
coherence

1910. Einstein : Induced em / short pulse
1950. Townes : maser concept
1958. Schawlow / Townes laser concept
1960. Maiman ruby laser

high power
high energy
(density
PW 10^{15} W)
high fields
↓
nonlinear effects

Key elements :

Induced emission of radiation – amplifier
Electromagnetic mode selection – resonator

Foundation :

Quantum theory of light matter interaction

Photonics

Wave nature of light

Maxwell equations → electromagnetic waves →
→ interaction with materials

Maxwell equations:

$$\left.\begin{array}{ll}\underline{E} & \text{electric field vector} \\ \underline{B} & \text{magnetic field vector}\end{array}\right\} \text{produce forces}$$

Materials characterized by

ρ charge density
$\underline{P}$ polarization (electric dipole mom. / unit value)
$\underline{M}$ magnetisation (magnetic —‖—)
$\underline{j}$ current density (current / unit area)

Lorentz force law: $\underline{F} = q\,(\underline{v} \times \underline{B})$
Ohm's law: $\underline{j} = \sigma \underline{E}$ (σ conductivity)

Electric und magnetic field in materials

- Dielectric material → $\exists \underline{P}$ $D\left[\frac{C}{m^2}\right]$ $E\left[\frac{V}{m}\right]$

  $\underline{D} = \varepsilon_0 \underline{E} + \underline{P}$ electric displacement
  in vacuum $\underline{D} = \varepsilon_0 \underline{E}$, $\varepsilon_0 = 8.9 \cdot 10^{-12} \frac{F}{m}$ vacum permittivity
  in material $\underline{D} = \varepsilon \underline{E} \rightsquigarrow \underline{P} = (\varepsilon - \varepsilon_0)\,\underline{E} = \chi \varepsilon_0 \underline{E}$
  $\chi = \frac{\varepsilon}{\varepsilon_0} - 1$ electric susceptibility

- Magnetic material → $\exists M$

  $\underline{B} = \mu_0 (\underline{H} + \underline{M})$ $\underline{H}$ magnetic field strength
  in vacuum $\underline{B} = \mu_0 \underline{H}$, $\mu_0 = 4\pi \cdot 10^{-7} \frac{H}{m}$ vacuum permittivity
  in material $\underline{B} = \mu \underline{H}$
  $\underline{E}, \underline{D}, \underline{B}, \underline{H}\ (x, y, z, t)$ $H\left[\frac{A}{m}\right]$

  $B[T]$
  $\downarrow$
  $\frac{Vs}{m^2}$

Field analysis ⟶ Fields (scalar / vector)

Scalar field $f(x,y,z)$ $\underline{\nabla}$ = del, nabla

Rate of change : gradient

$$\text{grad } f = \underline{\nabla} f = \frac{\partial f}{\partial x}\hat{\underline{i}} + \frac{\partial f}{\partial y}\hat{\underline{j}} + \frac{\partial f}{\partial z}\bar{\ell}$$ vector

Vector field $\underline{F}(x,y,z) = F_1(x,y,z)\hat{\underline{i}} + F_2(x,y,z)\hat{\underline{j}} + F_3(x,y,z)\hat{\underline{k}}$

Rate of change: scalar : divergence

vector : curl (rot)

– $$\text{div } \underline{F} = \underline{\nabla}\,\underline{F} = \frac{\partial F_1}{\partial x} + \frac{\partial F_2}{\partial y} + \frac{\partial F_3}{\partial z}$$

rate of change of matter at a point per unit volume per unit time (outflow – minus inflow)

– $$\text{curl } \underline{F} = \underline{\nabla}\times\underline{F} = \left(\frac{\partial F_3}{\partial y} - \frac{\partial F_2}{\partial z}\right)\hat{\underline{i}} - \left(\frac{\partial F_3}{\partial x} - \frac{\partial F_1}{\partial z}\right)\hat{\underline{j}} + \left(\frac{\partial F_2}{\partial x} - \frac{\partial F_1}{\partial x}\right)\hat{\underline{k}}$$

$$= \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ F_1 & F_2 & F_3 \end{vmatrix}$$

Shows the "rotational effects" of the field

direction of the curl vector ≡ axis of rotation

magnitude ≡ circulation density

$$\text{curl}(\text{curl } \underline{F}) = \underline{\nabla}\times(\underline{\nabla}\times\underline{F}) \equiv \text{grad}(\text{div } \underline{F}) - \Delta\underline{F} = \underline{\nabla}(\underline{\nabla}\,\underline{F}) - \underbrace{\underline{\nabla}^2}_{\text{Laplacian}}\underline{F}$$

$$\left(\underline{\nabla}^2\underline{F}\right)_{i=x,y,z} = \frac{\partial^2 F_i}{\partial x^2} + \frac{\partial^2 F_i}{\partial y^2} + \frac{\partial^2 F_i}{\partial z^2}$$

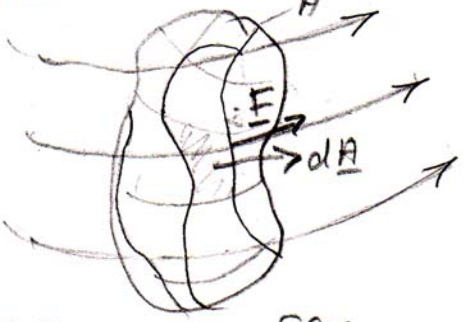
vector

Vector field theorems

Gauss theorem

Closed surface A, enclosed volume V

$\underline{F}(x, y, z)$



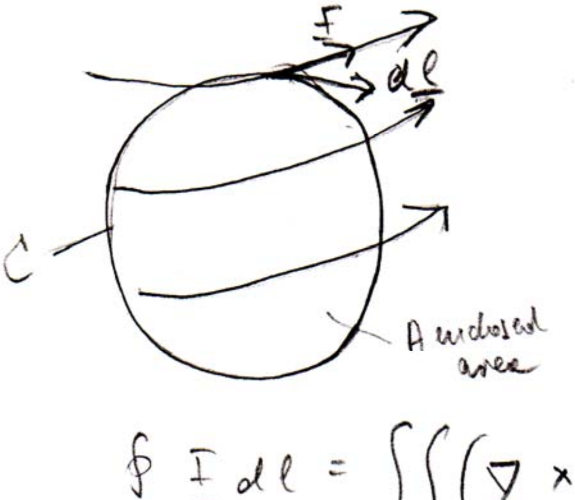
$$\oiint_A \underline{F}\, d\underline{A}$$

netto flux of $\underline{F}$ through A

$$\oiint_A \underline{F}\, d\underline{A} = \iiint_V \underline{\nabla} \cdot \underline{F}\, dV = \iiint_V \operatorname{div} \underline{F}\, dV$$

$$\underline{\nabla} = \left[\frac{\partial}{\partial x}\underline{x}, \frac{\partial}{\partial y}\underline{y}, \frac{\partial}{\partial z}\underline{z}\right]$$

Stokes theorem



Closed loop C

Netto circulation of $\underline{F}$ around C

$$\oint_C \underline{F}\, d\underline{l}$$

$$\oint_C \underline{F}\, d\underline{l} = \iint_A \left(\underline{\nabla} \times \underline{F}\right) d\underline{A} = \iint \underset{(\mathrm{rot})}{\operatorname{curl}} \underline{F}\, d\underline{A}$$

Electrodynamics

- Gauss's law

for a closed surface $\underset{A}{\oiint} \underline{E}\, dA = \frac{1}{\varepsilon_0} \underset{V}{\iiint} \varrho\, dV$

$\downarrow \qquad \parallel$

Gauss theorem → $\iiint \underline{\nabla}\, \underline{E}\, dV$

$\downarrow$

ε_0 vacuum permittivity

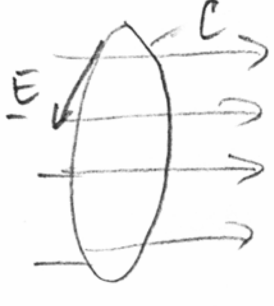
$$\rightsquigarrow \boxed{\underline{\nabla}\, \underline{E} = \frac{\varrho}{\varepsilon_0}}$$

- Biot-Savart law

Magnetic monopoles $\nexists$

$\underset{A}{\oiint} \underline{B}\, dA = 0 \qquad \rightsquigarrow \boxed{\underline{\nabla} \cdot \underline{B} = 0}$

- Faraday's law



B(t) increases

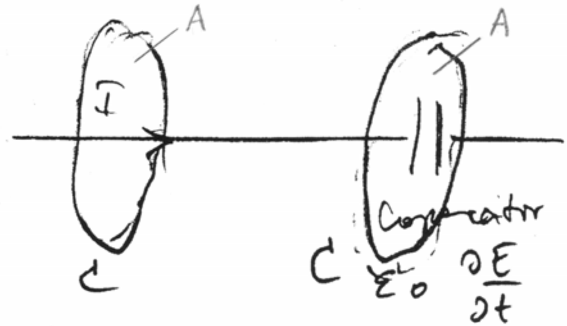
$$\underset{C}{\int} \underline{E}\, dl = -\frac{d}{dt} \underset{A}{\iint} \underline{B}\, d\underline{A}$$

$\swarrow \qquad \parallel$

Stokes theorem $\underset{A}{\iint} (\underline{\nabla} \times \underline{E})\, d\underline{A}$

$$\rightsquigarrow \boxed{\underline{\nabla} \times \underline{E} = -\frac{\partial \underline{B}}{\partial t}}$$

Ampere's law



μ_0 = vacuum perme

$$\int_C \underline{B}\, d\underline{l} = \mu_0 \iint_A \underline{j}\, d\underline{A} + \mu_0 \iint_A \varepsilon_0 \frac{d\underline{E}}{dt}\, d\underline{A}$$

$\downarrow$ Stokes theorem

$$\iint_A (\underline{\nabla} \times \underline{B})\, d\underline{A} = \mu_0 \iint_A \left(j + \varepsilon_0 \frac{d\underline{E}}{dt} \right) d\underline{A}$$

$$\boxed{\underline{\nabla} \times \underline{B} = \mu_0 \left(\underline{j} + \varepsilon_0 \frac{\partial \underline{E}}{\partial t} \right)}$$

☐ – 4 Maxwell equations

$q = 0 , \; j = 0$

Maxwell's wave equations in vacuum ≡ wave equation

in general: $\frac{\partial^2 A(x,t)}{\partial x^2} =\sim \frac{1}{v^2}\frac{\partial^2 A(x,t)}{\partial t^2}$

$\nabla \underline{E} = 0 \qquad \nabla\cdot\underline{H} = 0$

$\nabla\times\underline{E} = -\mu_0\frac{\partial \underline{H}}{\partial t} \qquad \underline{\nabla}\times\underline{H} = \varepsilon_0\frac{\partial \underline{E}}{\partial t}$

$\downarrow \qquad \downarrow$

$\underline{\nabla}\times \qquad \frac{\partial}{\partial t}$

$\underline{\nabla}\times(\underline{\nabla}\times\underline{E}) = -\mu_0\left(\underline{\nabla}\times\frac{\partial\underline{H}}{\partial t}\right) \qquad \left(\underline{\nabla}\times\frac{\partial\underline{H}}{\partial t}\right) = \varepsilon_0\frac{\partial^2\underline{E}}{\partial t^2}$ order of differentiation can be reversed

$\underline{\nabla}\times(\underline{\nabla}\times\underline{E}) = -\mu_0\varepsilon_0\frac{\partial^2\underline{E}}{\partial t^2}$ and (similarly)

$\underline{\nabla}\times(\underline{\nabla}\times\underline{H}) = -\mu_0\varepsilon_0\frac{\partial^2\underline{H}}{\partial t^2}$

However

$\underline{\nabla}\times(\underline{\nabla}\times\underline{A}) = \underline{\nabla}(\overset{0}{\overset{\parallel}{\underline{\nabla}\underline{A}}}) - \nabla^2\underline{A} \quad \longrightarrow$

$$\boxed{\underline{\nabla}^2\underline{E} = \mu_0\varepsilon_0\frac{\partial^2\underline{E}}{\partial t^2} \qquad \underline{\nabla}^2\underline{H} = \mu_0\varepsilon_0\frac{\partial^2\underline{H}}{\partial t^2}}$$ wave equation

Laplacism $(\underline{\nabla}^2\underline{E})_{i=x,y,z} = \frac{\partial^2 E_i}{\partial x^2} + \frac{\partial^2 E_i}{\partial y^2} + \frac{\partial^2 E_i}{\partial z^2}$ (same for $\underline{H}$)

$\underline{E}, \underline{H} \longrightarrow \underline{A} \qquad \underline{\nabla}^2\underline{A} = \frac{1}{v^2}\frac{\partial^2\underline{A}}{\partial t^2}$ wave equation

$v = (\mu_0\varepsilon_0)^{-1/2} = c \approx 3\cdot 10^8 \frac{m}{sec}$ velocity of the wave in vacuum

1 dimensional problem → wave propagating in the z direction

$$\frac{d^2A(z,t)}{dz^2} = \frac{1}{v^2}\frac{d^2A(z,t)}{dt^2}$$

Solution

$A(z,t) = A_z\cdot A_t \longrightarrow A_t\frac{d^2A_z}{dz^2} = \frac{A_z}{v^2}\frac{d^2A_z}{dt^2} = 0$

rearranging

$$\underbrace{\frac{v^2}{A_z}\frac{d^2A_z}{dz^2}}_{\text{z dependent}} = \underbrace{\frac{1}{A_t}\frac{d^2A_t}{dt^2}}_{\text{time dependent}} \rightsquigarrow = \text{hold both must be constant} : -\omega^2$$

$$\frac{d^2A_z}{dz^2} + \frac{\omega^2}{v^2}A_z = 0 \qquad \frac{d^2A_t}{dt^2} + \omega^2 A_t = 0$$

Solutions:

$$A_z = C_1 e^{i\left(\frac{\omega}{v}\right)z} + C_2 e^{-i\left(\frac{\omega}{v}\right)z}$$

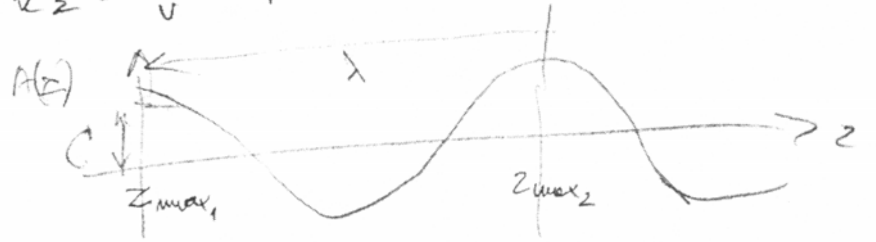
$$A_t = D_1 e^{i\omega t} + D_2 e^{-i\omega t}$$

wave travelling from left to right

$$A(z,t) = C e^{-i\left(\frac{\omega}{v}z - \omega t\right)} = C e^{-i(k_z z - \omega t)}$$

$k_z = \frac{\omega}{v}$ propagation constant or wave number

Between two max $\Delta\phi = 2\delta$



$$\frac{\omega}{v}\underbrace{\left(z_{max_1} - z_{max_2}\right)}_{\lambda} = 2\pi$$

$$2\pi\nu \cdot \lambda = v \cdot 2\pi$$

$$\underline{\nu \cdot \lambda = v}$$

$\underline{|t \text{ fixed}}$ ↑ λ = distance between successive maxima

$$v = \lambda\nu \qquad \nu = \frac{\omega}{2\pi} \qquad \longrightarrow k_z = \frac{2\pi}{\lambda} = \frac{\omega}{v}$$

The phase of the wave $\phi = k_z z - \omega t$

- Phase velocity $\phi = \text{const.} \rightsquigarrow d\phi = 0 \rightsquigarrow k_z dz - \omega dt = 0$

$$v_{phase} = \frac{dz}{dt} = \frac{\omega}{k_z} = \frac{1}{\sqrt{\varepsilon_0\mu_0}} \quad \text{in vacuum} \quad \equiv c$$

- Group velocity
  wave frequency in range $\Delta\omega$ around ω_0

$$E(z,t) = \int E(\omega) e^{-i(kz - \omega t)} d\omega \qquad (\text{Fourier expansion})$$

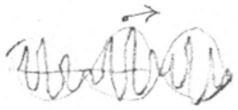
k(ν) may be frequency dependent (in material)

$k = k_0 + \frac{dk}{d\omega}(\omega - \omega_0)_{\Delta\omega/2}$ to 1. order

$E(z,t) = e^{-i(k_{z0} z - \omega t)} \int_{-\Delta\omega/2} E(\omega) \exp\left\{-i\left[\left(\frac{dk}{d\omega}\right)_{\omega_0} z - t\right]\Delta\omega\right\} d\Delta\omega$

$\Delta\omega = \omega - \omega_0$

plane wave



modulation | phase of modulation $\psi = \frac{dk}{d\omega} z - t = \text{const}$

$d\psi = 0 \rightarrow \frac{dk}{d\omega} dz - dt = 0 \rightarrow v_g = \frac{dz}{dt} = \boxed{\frac{d\omega}{dk}}$

$v_g \neq v_{ph}$ in dispersive medium ($v_{ph} = v_{ph}(\lambda)$) $k = k(\omega)$

- Generalized wave in 3 dimensions, polarized light

$\underline{E} = \underline{E}_0 e^{-i(\underline{k}\,\underline{r} - \omega t)}$ similar for $\underline{H}$

- Transverse electromagnetic waves and polarized light

$\underline{\nabla} \cdot \underline{E} = \text{div}(\underline{E}) = \left[\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z}\right] = 0$

$\underline{\nabla}\underline{E} = i\underline{k}\,\underline{E} = 0 \rightarrow \underline{k} \perp \underline{E}$

$\underline{\nabla} \cdot \underline{H} = 0 \rightarrow \underline{k} \perp \underline{H}$ also $\underline{E} \perp \underline{H}$

transverse waves

linear polarization
circular polarization
elliptical polarization
random polarization

- Flow of energy

Poynting vector $\underline{S} = \underline{E} \times \underline{H}$ average value $\langle \underline{S} \rangle = \frac{1}{2} \underline{E}_0 \times \underline{H}$

Electromagnetic waves in materials

$\varepsilon_0 \to \varepsilon$ $\qquad \mu_0 \to \mu$ $\qquad \rightsquigarrow v = (\mu\varepsilon)^{-1/2} = \frac{c}{n}$

susceptibility $\qquad$ permeability

n = index of refraction $= \sqrt{\frac{\varepsilon}{\varepsilon_0} \cdot \frac{\mu}{\mu_0}} \approx \sqrt{\frac{\varepsilon}{\varepsilon_0}}$ · for dielectric

↖ relative permittivity

Maxwell eq. and wave eq. in medium

$$\underline{\nabla} \cdot \underline{E} = -\frac{1}{\varepsilon_0} \underline{\nabla} \cdot \underline{P}$$

$$\underline{\nabla} \underline{H} = 0$$

$$\underline{\nabla} \times \underline{H} = \varepsilon_0 \frac{\partial \underline{E}}{\partial t} + \frac{\partial \underline{P}}{\partial t} + \underline{j} \quad \leftarrow \frac{\partial}{\partial t}$$

, eliminating $\underline{H}$

$$\underline{\nabla} \times \underline{E} = -\mu_0 \frac{\partial H}{\partial t} \qquad \leftarrow \text{curl}$$

$$\underline{\nabla} \times (\underline{\nabla} \times \underline{E}) = -\frac{1}{c^2} \frac{\partial^2 \underline{E}}{\partial t^2} - \mu_0 \frac{\partial^2 \underline{P}}{\partial t^2} - \mu_0 \frac{\partial \underline{j}}{\partial t}$$

dielectric (localized change effects) $\qquad$ conductor / semiconductor (absorption)

Induced polarization

no conduction but macroscopic polarization $\underline{P} = -Ne\underline{x}$

$\qquad\qquad$ ↓ number of displaced changes/unit volume

$-e\underline{E} = k\underline{x}$ $\quad$ restoring force $\rightsquigarrow \underline{P} = \frac{Ne^2}{k}\underline{E}$

↓ "spring $\qquad$ for static field

for time varying field

$$m \ast \frac{d^2x}{dt^2} + m\gamma \frac{dx}{dt} + kx = -e\underline{E} \qquad \text{damped harmonic osc.}$$

$\frac{1}{\gamma} = \tau$ = polarization decay time

$$\underline{E} = \underline{E}_0 e^{i\omega t} \to \underline{x} = \underline{x}_0 e^{i\omega t}$$

$$(-m\omega^2 - i\omega m\gamma + k)\underline{x} = -e\underline{E}$$

with this $\underline{x}$ $\quad \underline{P} = -Ne\underline{x}$

$$\underline{P} = \left(\frac{Ne^2}{-m\omega^2 - i\omega m\gamma + k}\right)\underline{E}$$

resonance frequency $\quad \omega_0 = \sqrt{\frac{k}{m}}$

$$\underline{P} = \frac{Ne^2}{\omega_0^2 - \omega^2 - i\omega\gamma}\underline{E}$$

Introducing it to the maxw. $\underline{\nabla}\times\underline{\nabla}$ eq.

$$\underline{\nabla}\times(\underline{\nabla}\times\underline{E}) + \frac{1}{c^2}\frac{\partial^2 \underline{E}}{\partial t^2} = -\frac{\mu_0 Ne^2}{m}\left(\frac{1}{\omega_0^2-\omega^2-i\gamma\omega}\right)\frac{\partial^2\underline{E}}{\partial t^2} \qquad (j=0)$$

$$\downarrow$$

$\underbrace{\nabla(\nabla E)}_{0} - \underline{\nabla}^2\underline{E}$ (because for spatially uniform medium $\underline{\nabla}\cdot\underline{P} = \underline{\nabla}\underline{E} = 0$)

$$\underline{\nabla}^2\underline{E} = \frac{1}{c^2}\left(1+\frac{Ne^2}{m\varepsilon_0}\left[\frac{1}{\omega_0^2-\omega^2-i\gamma\omega}\right]\right)\frac{\partial^2\underline{E}}{\partial t^2}$$

Solution:

$\underline{E} = E_0 e^{i(K_z\cdot z-\omega t)}$ $\qquad K_z$ complex propagation const.

Substituting:

$$K_z^2 = \frac{\omega^2}{c^2}\left(1+\frac{Ne^2}{m\varepsilon_0}\left[\frac{1}{\omega_0^2-\omega^2-i\gamma\omega}\right]\right)$$

$K_z = k_z + i\alpha_E \leftarrow$ extinction index for the amplitude for the energy $|E|^2 \sim e^{-2\alpha_E z}$

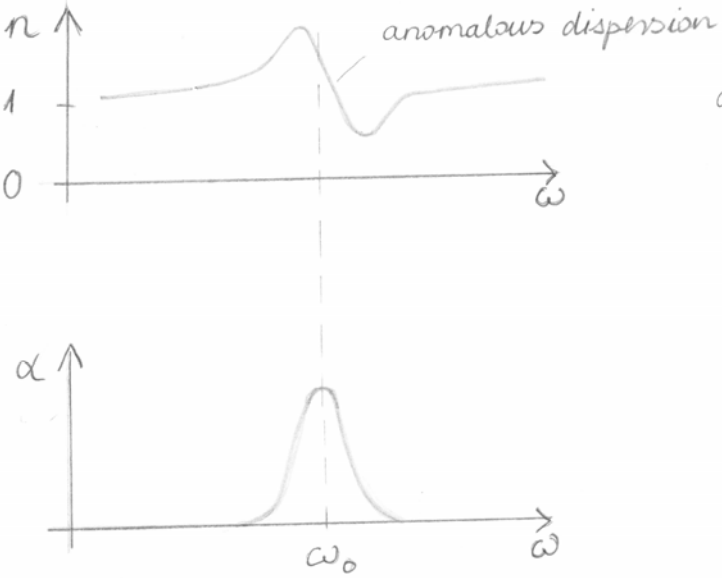
$\alpha = 2\alpha_E$ absorption coefficient

$$\underline{E} = \underline{E}_0 e^{-\alpha_E z} e^{i(k_z z-\omega t)}$$

From $K_z \rightarrow$ complex index of refraction

$\mathcal{N} = \frac{c}{\omega}K_z = n + i\varkappa \rightarrow \alpha_E = \frac{\omega}{c}\varkappa \quad \alpha = \frac{2\omega}{c}\varkappa$

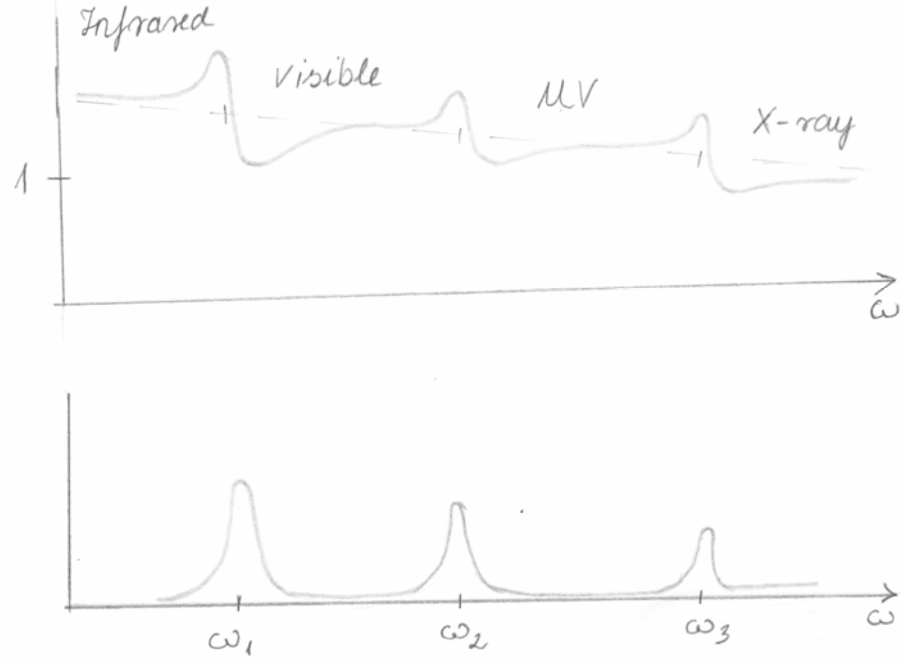
$v_{phase} = \frac{dz}{d\epsilon} = \frac{c}{n}$



dispersion curve

Real materials, multiple electrons, multiple spring constants, → multiple resonance frequencies ω_i,
dampings γ_j
relative oscillator strengths f_j

$$N^2 = 1 + \frac{Ne^2}{m\varepsilon_0}\sum_i \left(\frac{f_i}{\omega_i^2-\omega^2-i\gamma_i\omega}\right)$$



$$E(z,t) = Ce^{-eik(k_z z - \omega t)}$$

Group Velocity

Wave frequency in the range $\Delta\omega$ around ω_0

$$E(x,t) = \int E(\omega) e^{-i(kx - \omega t)} \, d\omega$$

(Fourier expension)

Superposition of waves

$E_1 = Ae^{-i(kx-\omega t)}$ $\qquad$ $E_2 = Ae^{-i(kx-\omega t+\phi)}$

$$E = E_1 + E_2 = Ae^{-i(kx-\omega t)}\underbrace{\left(1+e^{-i\phi}\right)}$$

$$\text{factoring: } e^{-i\frac{\phi}{2}}\underbrace{\left(e^{i\frac{\phi}{2}}+e^{-i\frac{\phi}{2}}\right)}_{2\cos\frac{\phi}{2}}$$

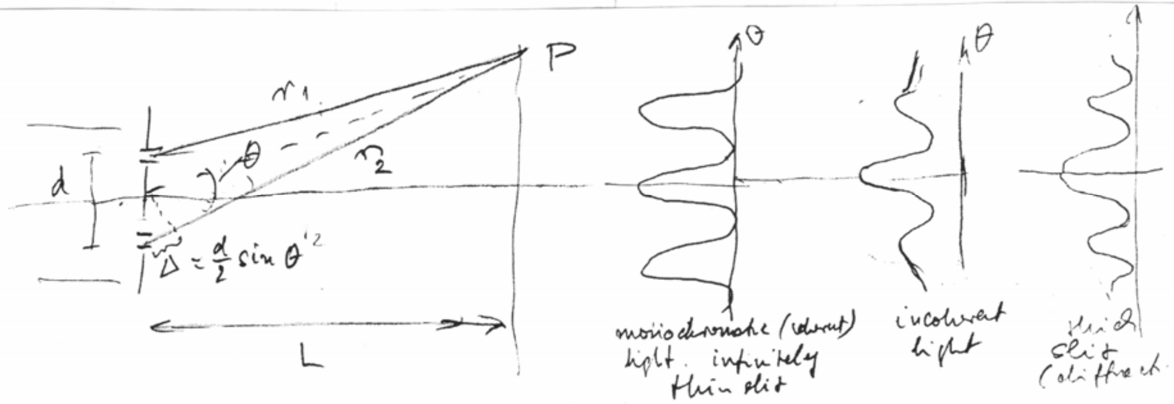
$$= Ae^{-i(kx-\omega t)} \cdot 2\cos\frac{\phi}{2} \cdot e^{-i\frac{\phi}{2}}$$

$I = E \cdot E^* = 4A^2\cos^2\left(\frac{\phi}{2}\right)$

$I = 4A^2$ when $\phi = 2m\pi$ constructive interference

$I = 0$ when $\phi = (2m+1)\pi$ destructive interference

Interface by division of wavefront



$E = A\left(e^{-ikr_1} + e^{-ikr_2}\right)e^{i\omega t}$

when L is large path difference $\overset{\text{OPD} = 2\Delta}{\approx} d\cdot\sin\theta \rightarrow$ phase diff. $\phi = kd\sin\theta =$

$= \frac{2\pi}{\lambda}d\sin\theta$

$I = 4A^2\cos^2\left(\frac{\pi}{\lambda}d\sin\theta\right)$

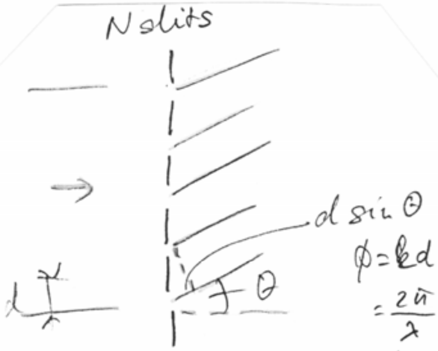
$\text{OPD} = m\lambda$ constructive $\qquad$ $\text{OPD} = \left(m+\frac{1}{2}\right)\lambda$ destructive interference

Thickness of hair:

Meas: $2\theta = \frac{10\text{ mm}}{10\text{ m}} = 10^{-2}$ $\quad \cos^2\theta = 0 \Rightarrow \phi = \frac{\pi}{2}$ $\quad$ between 2-0 points $\Delta\phi = \pi$

$$\frac{2\pi}{\lambda}d\underset{\substack{\downarrow\\10^{-2}}}{\sin\theta} = \pi \rightarrow 2d\cdot 10^{-2} = \lambda \rightarrow d = \frac{\lambda}{2}\cdot 10^{2} = \frac{0{,}5\,\mu m}{2}\cdot 10^{2} = 25\,\mu m$$

Multiple slit interference



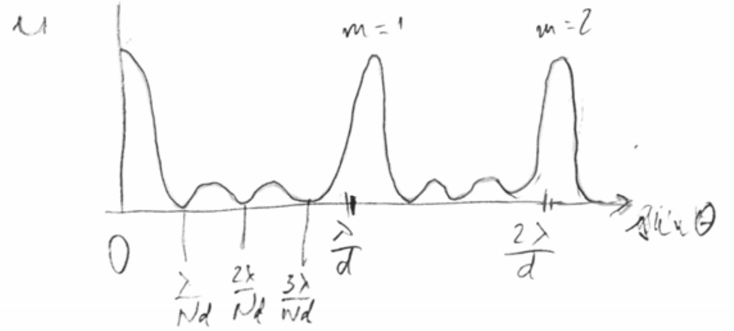
$\phi = kd\sin\theta = \frac{2\pi}{\lambda} d\sin\theta$

$$E = A e^{-ikr_1}\underbrace{\left[1 + e^{-i\phi} + e^{-i2\phi} + \dots e^{-i(N-1)\phi}\right]}$$

$$\frac{1-e^{-iN\phi}}{1-e^{-i\phi}} = \qquad \text{factor } \frac{e^{-iN\frac{\phi}{2}}}{e^{-i\frac{\phi}{2}}}$$

$$= e^{-i(N-1)\frac{\phi}{2}} \frac{\sin N\frac{\phi}{2}}{\sin\frac{\phi}{2}}$$

$$I(\theta) = A^2 \frac{\sin^2 N\frac{\phi}{2}}{\sin^2\frac{\phi}{2}} = A^2 \frac{\sin^2\frac{\pi}{\lambda} Nd\sin\theta}{\sin^2\frac{\pi}{\lambda} d\sin\theta}$$



Maxima

$\frac{\pi}{2} d\sin\theta = m\pi$

$m = 0, \pm 1, \pm 2 \dots$

$m\lambda = d\sin\theta$

principal maxima

Dispersion:

$$\sin\theta = \frac{m\lambda}{d} \qquad \cos\theta\Delta\theta = \frac{m}{d}\Delta\lambda \rightsquigarrow \frac{\Delta\theta}{\Delta\lambda} = \frac{m}{d\cos\theta}$$

increases with m!
linear with θ

Resolving power

$\lambda + \Delta\lambda$: maximum ≡ first minimum

$$\Delta\sin\theta = \frac{m\Delta\lambda}{d} \qquad \Delta\sin\theta = \frac{\lambda}{Nd} \rightarrow \frac{\lambda}{\Delta\lambda} = N\cdot m$$

N large!

Spectroscopy

Coherence : fixed phase relationship at the source

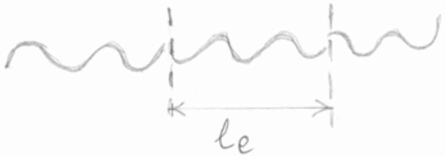
temporal coherence $I = I_1 + I_2 + 2E_1E_2 \cos \underset{\substack{\downarrow \\ \text{constant}}}{\theta}$

$$\theta = (k_1 - k_2)z + (\omega_1 - \omega_2)t + \varphi$$

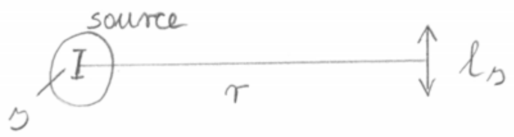
$$l_c = \frac{c}{\Delta\nu}$$

spectral lamp Hg $\Delta\nu = 10^9\,\text{Hz}$ $l_c = 0{,}5\,m$

He Ne laser $\Delta\nu = 10^6\,\text{Hz}$ $l_c = 300\,m$



Spatial coherence

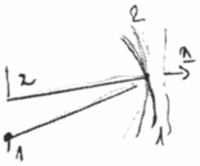


$$l_s = \frac{r\lambda}{s} = \frac{\lambda}{\theta_s}$$

laser : $\frac{6 \cdot 10^{-4}\,mm}{2 \cdot 10^{-3}} = 0{,}3\,mm$

lamp $= \frac{6 \cdot 10^{-4}\,mm}{1\,rad} = 6 \cdot 10^{-4}\,mm =$

$= 0{,}6\,\mu m$



$$E(T) = \iiint F(M)\, \frac{\partial}{\partial n}\left(\frac{e^{-jk\overline{PM}}}{\overline{PM}}\right) d\sigma\, dn$$

$$= \iiint F(M)\, \frac{\partial}{\partial PM}\left(\frac{e^{-jk\overline{PM}}}{\overline{PM}}\right) \frac{d\overline{PM}}{\partial n}\, d\sigma\, du =$$

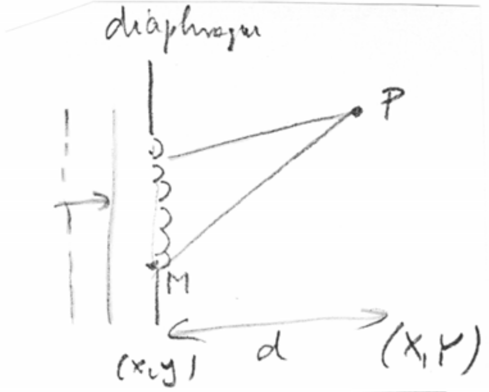
$$\iiint F(M)\left(\frac{jke^{jk\overline{PM}}}{PM} - \frac{e^{jkPM}}{PM^2}\right) \underbrace{\frac{\partial \overline{PM}}{\partial n}}_{(\cos n, r)} d\sigma\, du \qquad r = \overline{PM}$$

$$= \iiint F(M) \cdot \frac{e^{jk\overline{PM}}}{\overline{PM}} \left(jk - \underbrace{\cancel{\frac{1}{\overline{PM}}}}_{\text{ignore}}\right) \underbrace{\cos(n, r)}_{1}\, d\sigma\, du$$

$$\int du = 2\pi$$

$$\underbrace{2\pi jk}_{\frac{j}{\lambda}} \iint F(M) \frac{e^{jk\overline{PM}}}{PM}\, d\sigma$$

Huygens - Fresnel principle



$$dE(P) = F(M) \cdot \frac{e^{-jk\overline{PM}}}{\overline{PM}} d\sigma$$

$$E(P) = \frac{j}{\lambda} \iint_{\text{diaphragm}} F(M) \frac{e^{-jk\overline{PM}}}{\overline{PM}} d\sigma$$

$$PM = \sqrt{d^2 + (X-x)^2 + (Y-y)^2} = d \cdot \sqrt{1 + \left(\frac{X-x}{d}\right)^2 + \left(\frac{Y-y}{d}\right)^2} \approx d \cdot \left[1 + \frac{1}{2}\left(\frac{X-x}{d}\right)^2 + \left(\frac{Y-y}{d}\right)^2\right]$$

let $d \gg (X-x)$ and $(Y-y)$ $\overline{PM} \approx d$

$$E(x,Y) = \frac{j^{-jkd}}{\lambda d} \iint f(x,y)\, e^{-j\frac{k}{2d}\left[(X-x)^2 + (Y-y)^2\right]} dx dy$$

when $d \to \infty$

$$\frac{X}{d} = u, \quad \frac{Y}{d} = v \qquad \frac{x^2}{d}, \frac{y^2}{d} \to 0$$

then $\frac{(X-x)^2 + (Y-y)^2}{d} = \frac{X^2+Y^2}{d} - 2(ux - vy)$

$$E(X,Y) = \frac{j}{\lambda d} e^{-jkd} e^{-jk\frac{X^2+Y^2}{d}} \underbrace{\iint f(x,y)\, e^{-jk(ux+vy)} dx dy}_{\text{F.T.}\{f(x,y)\}\ !}$$

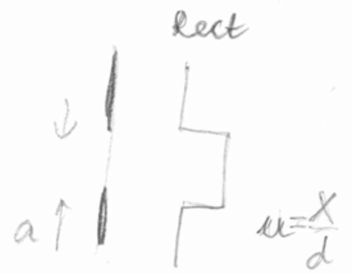
Fresnel diffraction

$\frac{X^2+Y^2}{d} \longrightarrow 0 \longrightarrow$ Fraunhofer diffraction far field
focal plane of a lens

u, v – angle - angular spectrum

Diffraction by a slit

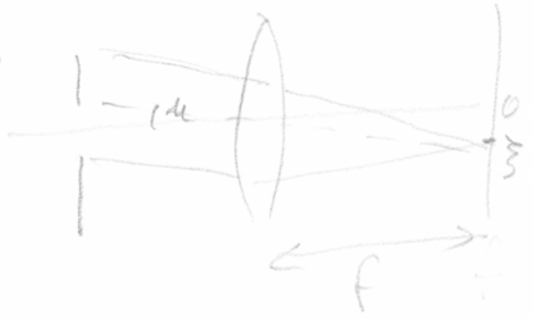
$$\mathrm{Rect}\left(\frac{x}{a}\right) = \begin{cases} 1 & |x| \le \frac{a}{2} \\ 0 & |x| \ge \frac{a}{2} \end{cases}$$



$$E(u) = \mathrm{F.T.}\left\{\mathrm{Rect}\left(\frac{x}{a}\right)\right\} = \frac{\sin(kau/2)}{kau/2} = \mathrm{sinc}\,\frac{kau}{2}$$

$$\underline{I} = I_0\,\mathrm{sinc}^2\,\frac{kau}{2}$$

Lens



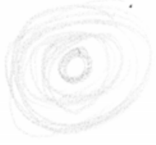
$u = \frac{\xi}{f}$ (small angle)

$$I = I_0\,\mathrm{sinc}^2\left(\frac{ka\xi}{2f}\right)$$

Circular aperture

$$C(x,y) = \begin{cases} 1 & (x^2+y^2) \le a^2 \\ 0 & (x^2+y^2 > a^2 \end{cases}$$

$$E(u,v) = \mathrm{F.T.}\{C(x,y)\} = \frac{2J_1(Z)}{Z} \qquad Z = 2\pi\frac{a}{\lambda}\sqrt{u^2+v^2}$$

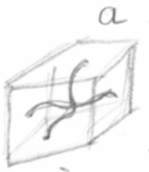
Airy disc  radius of first minimum

$$q = 1{,}22\,\frac{\lambda}{2a}\,f$$

(Resolving power)

Grating

Black body radiation in thermal equilibrium



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

1 dim.

$$n \cdot \frac{\lambda_n}{2} = L$$

$$\frac{c}{\nu_n} = \frac{2L}{n}$$

$$\nu_n = \frac{n \cdot \ell}{2L}$$

$$\nu < \nu_{max} \rightsquigarrow n_x^2 + n_y^2 + n_z^2 \leq \frac{4a^2 \nu_{max}^2}{c^{\cancel{3}2}}$$

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

$$\frac{1}{8}\left(\frac{4\pi}{3} R^3\right) = \underbrace{\frac{4\pi}{3} \frac{a^3 \nu_{max}^3}{c^3}}_{\text{number of modes}}$$

Class. Energy $\forall$ modes

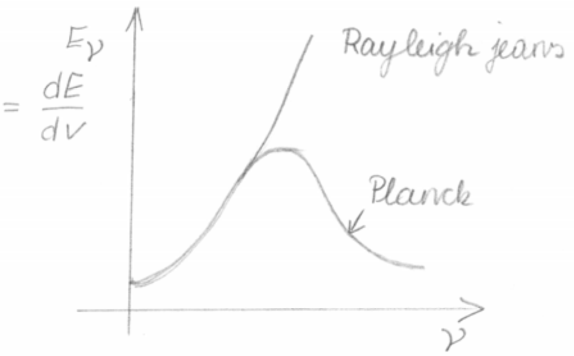
$$0 - \nu_{max} \text{ ig} : E_{\nu_{max}} = \frac{4\pi}{3} V \frac{\nu_{max}^3}{c^3} \cdot kT$$

$$E_\nu = \frac{4\pi V}{3c^3} \nu^2 d\nu \cdot kT$$

Rayleigh - jeans $\nu_{max} \to \infty$ Energy $\to \infty$

Planck: $N \cdot h\nu$ (energy of mod.)

$$E_\nu = \frac{4\pi V}{3c^3} \nu^2 \frac{h\nu}{e^{h\nu/kT} - 1} d\nu$$



Assumption $\varepsilon_n = n \cdot \varepsilon_0$

In thermal equilibrium: no. of particles with ε_n

$$N_n = N \cdot \frac{e^{-\frac{\varepsilon_n}{kT}}}{\sum_{n=0}^{\infty} e^{-\frac{\varepsilon_n}{kT}}} \qquad k = 1{,}38 \cdot 10^{-23} \frac{J}{{}^\circ K}$$

(Boltzmann constant)

Total energy of the system of N "particles":

$$E = \sum_{n=0}^{\infty} \varepsilon_n N_n = N \cdot \frac{\sum_{n=0}^{\infty} \varepsilon_n e^{-\frac{\varepsilon_n}{kT}}}{\sum_{n=0}^{\infty} e^{-\frac{\varepsilon_n}{kT}}}$$

$$= \frac{\frac{\partial}{\partial(-\frac{1}{kT})} \text{(geom. series)}}{\text{(geom. series)}} = N \frac{\varepsilon_0}{e^{-\varepsilon_0/kT} - 1}$$

$$e^{-\frac{\varepsilon_0}{kT}} = 1 + \frac{\varepsilon_0}{kT} + \frac{\varepsilon_0^2}{2k^2T^2} + \dots$$

$$E = N \cdot \frac{\varepsilon_0}{\left(1 + \frac{\varepsilon_0}{kT} + \frac{\varepsilon_0^2}{2k^2T^2} + \dots\right) - 1} = N \cdot \frac{kT}{1 + \frac{\varepsilon_0}{2kT} + \dots}$$

$\varepsilon_0 \to 0 \quad \rightsquigarrow \quad E = NkT$

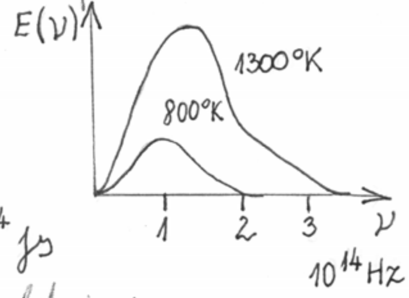
$\overline{\varepsilon} = kT \quad \rightsquigarrow$ Rayleigh Jeans

$\varepsilon_0 \not\to 0 \quad \rightsquigarrow \quad \overline{\varepsilon} = \frac{E}{N} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$ Planck

$\varepsilon_0 = h\nu \quad h = 6{,}6 \cdot 10^{-34}$ Jsec (Planck constant)

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

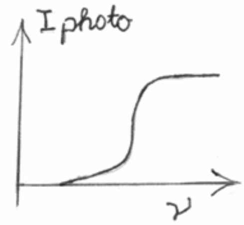
$$E(\nu) = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}$$ $h = 6{,}6 \cdot 10^{-34}$ Js

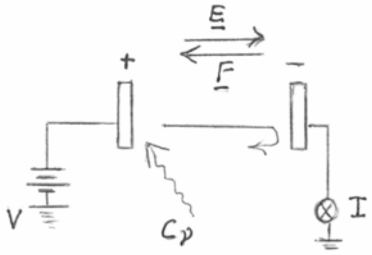
Wien : $\lambda_{max} \cdot T = \text{const.}$

Stefan - Boltzm :

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

- Photoelectric effect





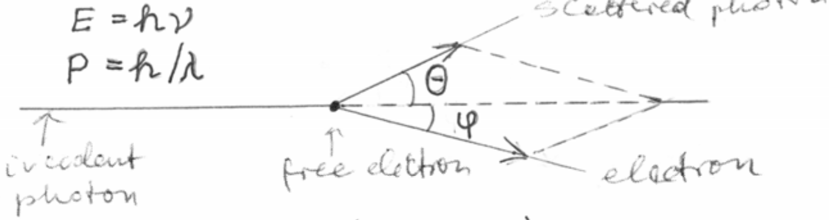
I = 0 at $V = V_0$

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

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 /

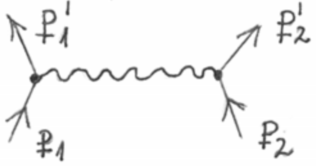
$$\lambda_C = \frac{h}{m_e \cdot c}$$

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

- 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

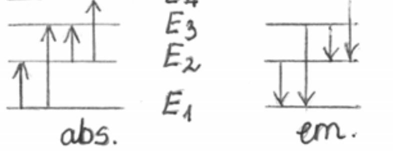
System of charged particles: atom, molecule, nucleus etc.

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

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

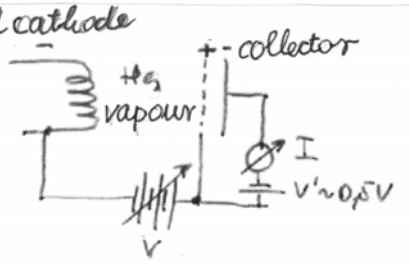
Disreet energy levels → stationary states

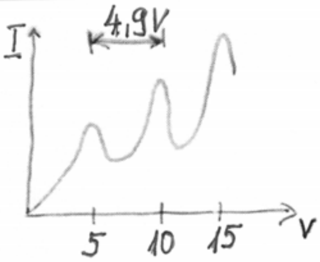
$A + h\nu \longrightarrow A^*$ abs.
$A^* \longrightarrow A + h\nu$ em.



- Contradiction with classical mechanics
  quantization of energy
  electron circulates but does not radiate

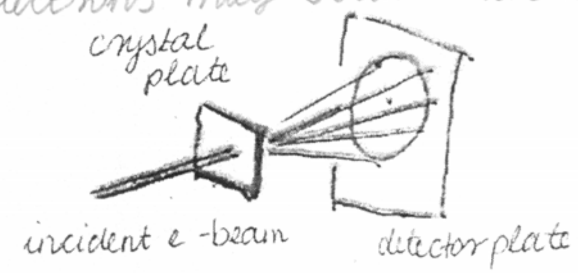
Franck-Hertz experiment

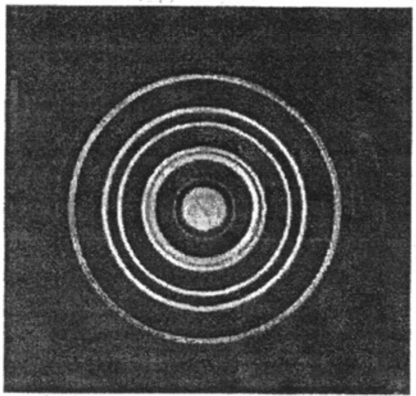




- Wave particle dualing

Electrons may behave like waves: interference, diffr.





Diffraction image
(powdersample)

de Broglie wavelength $E=\frac{p^2}{2m_e}=eV \rightsquigarrow p=\sqrt{2m_e\cdot eV}$

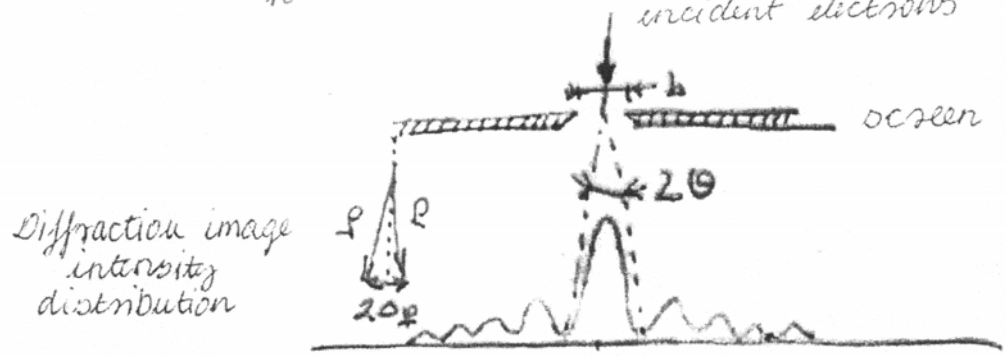
$$p=\frac{h}{\lambda} \rightsquigarrow \lambda=\frac{h}{\sqrt{2m_e\cdot eV}}$$

Free particle → wave packet

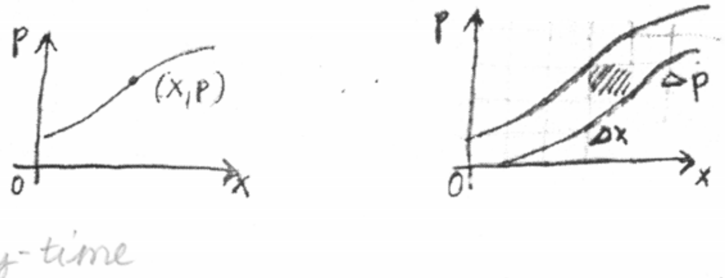
Heisenberg <u>uncertaining</u> relationship

wave packet → Fourier transform $\Delta x\cdot\Delta k=2\pi$

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



Motion in phase space:



Energy-time

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

$$\Delta t\cdot\Delta\omega\sim 2\pi \qquad \Delta\omega\,\frac{\Delta E}{\hbar}$$

Stationary state → lifetime → linewidth

Uncertainity relationship (Heisenberg)

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

Macroworld

e.g. $\Delta x = 1 \mu m = 10^{-6} \, m$

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

e.g. $m = 1 \mu g = 10^{-9} \, kg$

$$\Delta v = \frac{\Delta p}{m} = 6,6 \cdot 10^{-19} \, \frac{m}{s} \approx 0$$

Microworld

atom: $\Delta x \approx 0,1 \, nm \; (= 1 \text{Å}) = 10^{-10} \, m$

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

electron $m_{el} = 10^{-30} \, kg$

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

Quantum mechanics /2

Wave function, probability density, Schrödinger equation

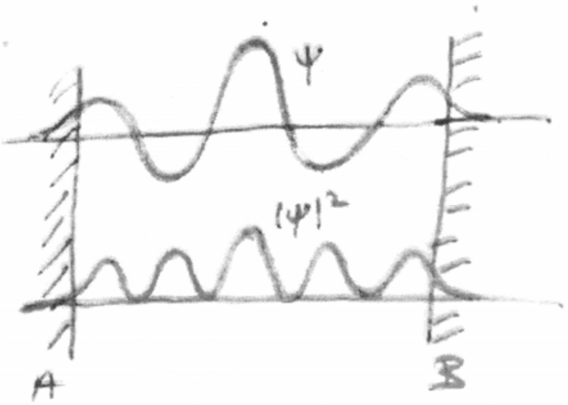
- Motion of particles
Classical orbit ↓
Localized particle - standing wave - wavefunction $\psi(x)$
Wave intensity $\sim |\psi|^2$
ψ complex ψ^* compl. conjugate $|\psi|^2 = \psi^* \psi$

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

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. 1 Probability distribu of electron positi in an atom

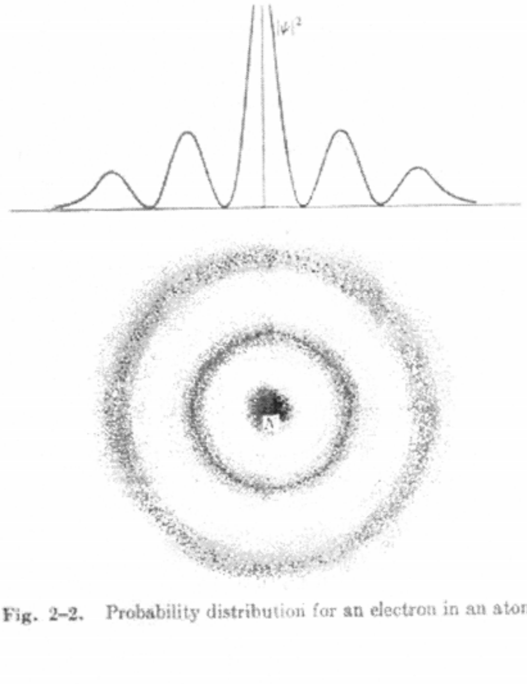


Fig. 2–2. Probability distribution for an electron in an atom.

- 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

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

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 (Compton) $p \overset{\wedge}{=} \hbar k$ $\left(p = \frac{h}{\lambda}\right)$ 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. $\psi(x) = e^{ikx} \rightarrow |\psi|^2 = 1$: 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 ($E_p(x)$)

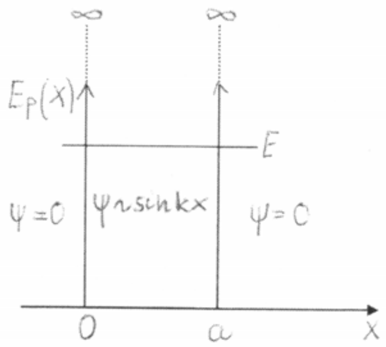
Potential box

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

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

$= \infty$ outside

$\rightsquigarrow \Psi(x) = 0$ outside



Inside:

Schr. e.: $\frac{d^2\Psi}{dx^2} + k^2\Psi = 0 \qquad k = \frac{p}{\hbar} = \frac{\sqrt{2mE}}{\hbar}$

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

$$\Psi(x) = A e^{ikx} + B e^{-ikx}$$

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

$\rightarrow \Psi(0) = A + B = 0 \quad \rightsquigarrow A = -B \rightsquigarrow$

$\Psi(x) = A(e^{ikx} - e^{-ikx}) = 2iA \sin kx = C' \sin kx \quad C = 2iA$

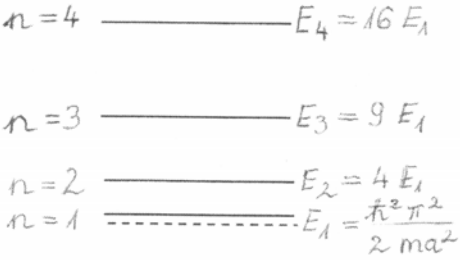
$\rightarrow \Psi(a) = C' \sin ka = 0 \quad \rightsquigarrow \sin ka = 0 \rightsquigarrow$

$k = \frac{n\pi}{a}$ $\underline{n = \text{integer!}}$ $\boxed{p = \hbar \frac{n\pi}{a} \text{ momentum}}$ quantized

The energy:

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} =$$

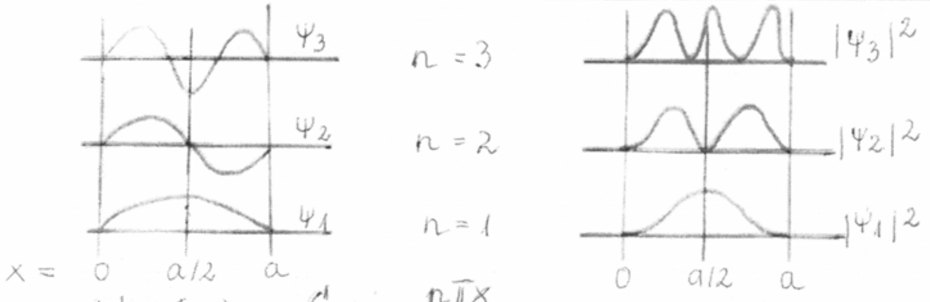
$$= \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad E_n \sim n^2$$



Discrete energy values

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

The wavefunctions and the probability densities



$E_3 = 9E_1$

$E_2 = 4E_1$

$E_1 = \frac{h^2}{2ma^2}$

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

The particle can exist only with energy larger than 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 0-point energy

It follows from Heisenberg's uncertainty principle

$\Delta x \, \Delta p \geq h$ now: $\Delta x \sim a \quad \Delta p \sim 2p$ (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 → from normalization

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

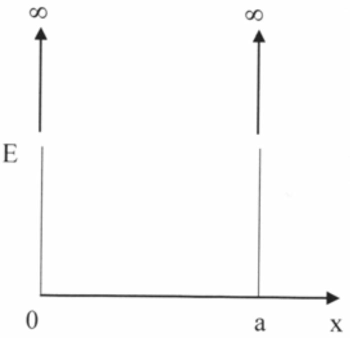
$$\psi_n(x) = \sqrt{\frac{2}{a}}\,\sin\frac{n\pi x}{a}$$

The wavefunctions are orthogonal i.e.

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

since

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



Wave – particle duality
wave function
Schrödinger eq.: $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + E_p\psi = E\psi$
Motion limited in space

1 dim

$E_n = \frac{\pi^2\hbar^2}{2ma^2} n^2 \qquad n = 1, 2, \dots$ energy discreet

$E_1 = \frac{\pi\hbar^2}{2ma^2}$ 0 point energy

$\psi_n = C \sin\frac{n\pi x}{a}$ discreet wave function

$C = \sqrt{\frac{2}{a}}$ ψ normalized

$\psi_n^* \psi_{n'} = \int_{-\infty}^{\infty} \psi_n^* \psi_{n'} = \begin{cases} 0 & n \neq n' \\ 1 & n = n' \end{cases}$ orthonormalized set of functions

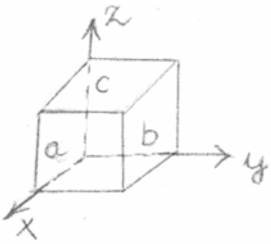
3 dim : degenerate states. E direction independent

degree of degeneracy $\longrightarrow$ density of states
between E, E+dE

$g(E) \sim E^{1/2}$

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

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

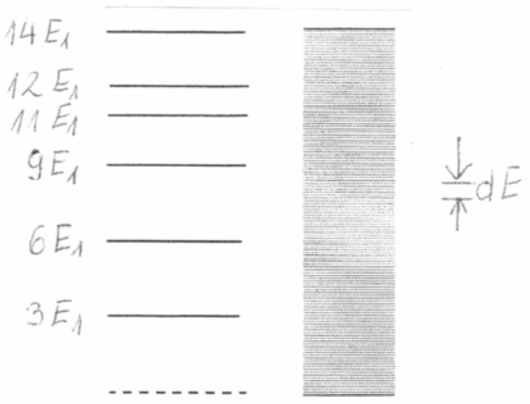
The same $\varkappa$ with different n_1, n_2, n_3 → <u>degeneracy</u>

Possible energy	n_1, n_2, n_3 combination	degree of degenerac (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

$$E_1 = \frac{\pi^2\hbar^2}{2ma^2}$$

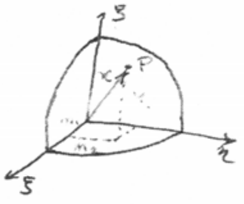
<u>Big box</u>

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



Number of states between 0 − E : N(E)

$\frac{1}{8}$ th of the volume of a sphere with radius $\kappa = \sqrt{\frac{2mE}{\pi^2 \hbar^2}} \cdot a$



$V = a^3$

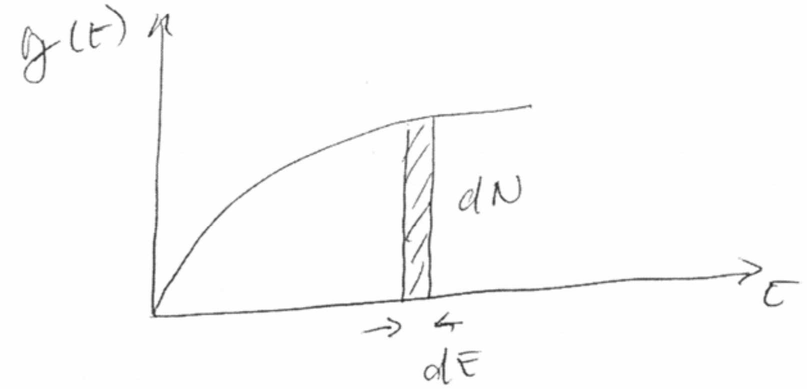
$$N(E) = \frac{1}{8}\ \frac{4\pi \kappa^3}{3} =$$

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

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

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

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

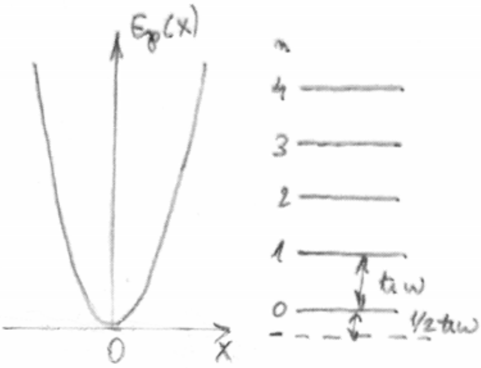
Schr. eq.

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

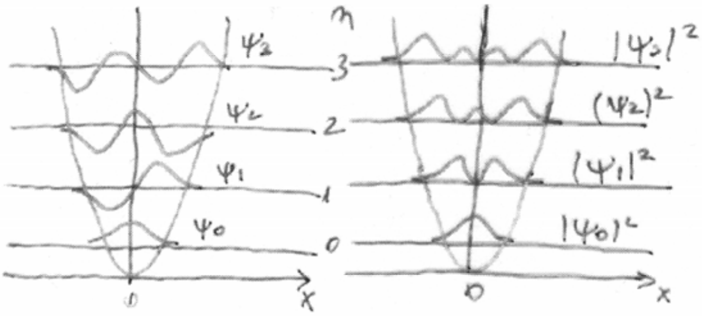
$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

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

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



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



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

In three dimensions spatial harmonic oscillator

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

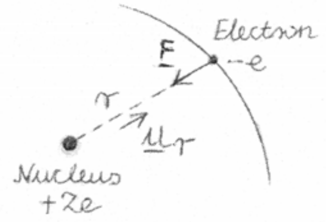
Atoms

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 ∖ Electromagnetic
- Z electrons with charge −e / interaction
- $m_{nucleon} \approx 1850\, m_{electron}$

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

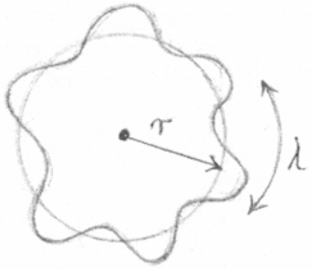
The potential energy: $E_p(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$ $\rightsquigarrow$

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

$r_n = \frac{n\lambda}{2\pi}$ $\underset{\substack{| \\ \text{ang. mom.}}}{L} = r \cdot p = \frac{n\lambda}{2\pi}\frac{h}{\lambda} = n\cdot\hbar$ $\left(p = \hbar k = \frac{h}{2\pi}\cdot\frac{2\pi}{\lambda} = \frac{h}{\lambda}\right)$

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

Classically: centripetal force $\equiv$ Coulomb attraction

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

$\rightsquigarrow r = \frac{n^2 \hbar^2 \epsilon_0}{\pi m_e Z e^2} = \frac{n^2}{Z} \cdot a_0$ $\quad a_0 =$ 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] $\quad \overset{\nearrow}{1{,}6 \cdot 10^{-19}\, J}$

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?

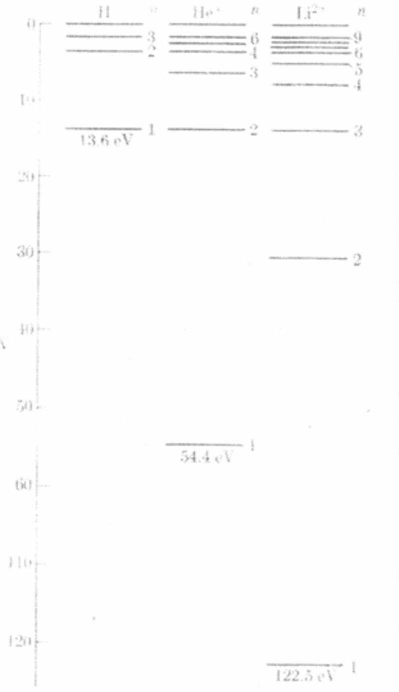
e.g. He^+ $n = 2, 4, 6$

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 radiaton 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

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

This is the Balmer formula

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

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

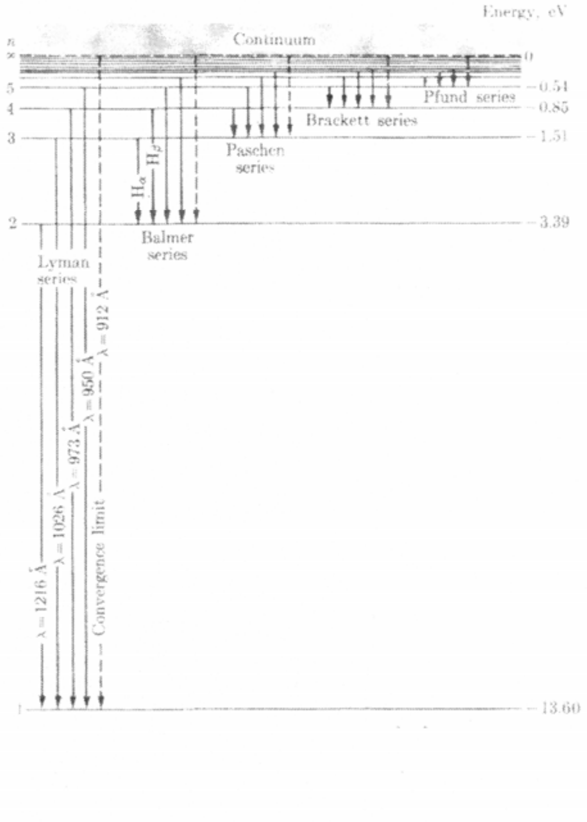
Spectral lines

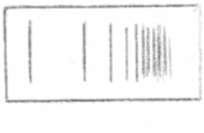
Series: joint lowest energy states

Balmer series: visible

Lyman series: UV

others: infra





Wave function

Solution of $\frac{d^2\xi}{dx^2} + k^2\xi = 0$, but $p = \hbar k$ (q.m.)

wave equation

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

But $p^2 = 2m[E - E_p(x)]$

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

$$\underbrace{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + E_p(x)\psi}_{\hat{E}\psi} = E\psi$$

$= E\psi$ eigenvalue eq. of $\hat{E}$ operator

$\boxed{\hat{E}\psi_n = E_n\psi_n}$ discreet

E = constant of motion

operator

these characterize the states

eigenfunctions — probability

eigenvalues — possible measurement results

Other physical quantities → simultaneous eigenfunction (when simultaneously measurable

If it is a constant of motion → operator

eigenvalues

eigenfunctions

(– convenience)

e.g. $\frac{p^2}{2m} \equiv -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \rightsquigarrow \hat{p} = -i\hbar\frac{d}{dx}$

3 dim : $p = -i\hbar\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) = -i\hbar\underline{\nabla}$

Spherically symmetric central field

$\underline{L} = \underline{r} \times \underline{p}$ — constant of motion / angular momentum

$\hat{L} = -i\hbar\,\underline{r} \times \underline{\nabla}$

$\hat{\underline{L}}\psi_k = L_k\psi_k$ discreet ψ_k, L_k ?

Spherically symmetric central force field

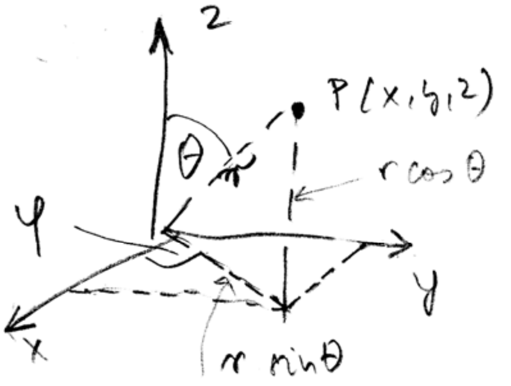
$E_p = E_p(\underline{r})$

Angular momentum $\underline{L} = \underline{r} \times \underline{p}$ is conserved

Quantum mechanics $p = -i\hbar \underline{\nabla}$

$\underline{L} \to \underline{\hat{L}} = -i\hbar\, \underline{r} \times \underline{\nabla}$ $L_x, L_y, L_z \to \hat{L}_x, \hat{L}_y, \hat{L}_z$

$x, y, z \to r, \theta, \varphi$ spherical coordinates



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

$\hat{L}_z = -i\hbar \frac{\partial}{\partial\varphi}$ $\hat{L}_z\psi = L_z\psi \to \frac{\partial\psi}{\partial\varphi} = i m_l \psi$

$\rightsquigarrow \psi = Ce^{im_l\varphi} = Ce^{im_l(\varphi+2\pi)} \to e^{i2\pi m_l} = 1 \to m_l = 0, \pm 1, \pm$

$\rightsquigarrow L_z = m_l \cdot \hbar$

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

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

$Y_{l,m_l} = P_l^{m_l}(\cos\theta)e^{im_l\varphi}$

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

Quantum mechanics / 5.

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

– 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~~ and L^2 (classically: direction and absolute value)

$$\hat{L} = -i\hbar\, \underline{r} \times \underline{\nabla} = -i\hbar \begin{vmatrix} \underline{u}_x & \underline{u}_y & \underline{u}_z \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$$

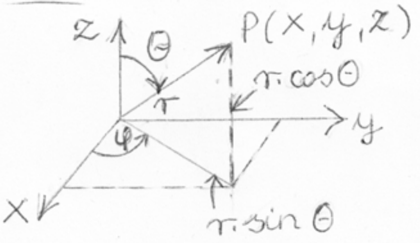
(determinant

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

$\hat{L}_x, \hat{L}_y$ 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 $\frac{\partial}{\partial\varphi}$ -

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

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

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

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

with $\frac{L_z}{\hbar} = m_e \longrightarrow \frac{\partial \psi}{\partial \psi} \, i m_e \psi$

Solution: $\psi = C e^{i m_e \varphi}$

But $\varphi \to \varphi + 2\pi$ ψ can not change $\rightsquigarrow$

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

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

$\psi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{i m_e \varphi}$ 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 $Y_{e,m_e} = P_e^{m_e}(\cos\theta)\, e^{i m_e \varphi}$

$\longrightarrow Y_{e,m_e}$ $\hat{L}^2$ 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 ⇝ $\left(E_n = \frac{13,6\, Z^2}{n^2}\right)$

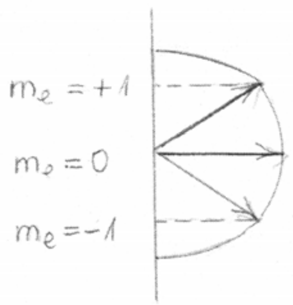
l can change between 0, ... (n−1)

The angle of the $\underline{L}$ vector with the z axis is discreet

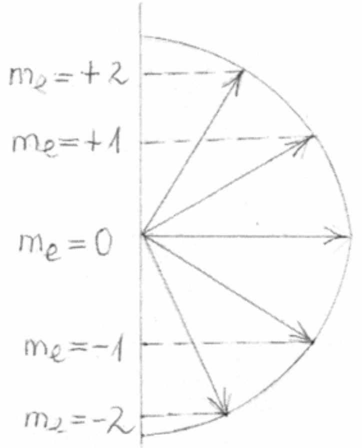
$L_z = m_l \cdot \hbar$

$m_l \le l$ 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

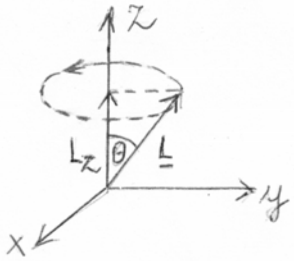
Only one component of the angular momentum vector $\underline{L}$ can be measured precisely

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 :

$|\underline{L}|$ 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

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

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

Tranfer 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 $\hat{L}^2$

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

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

Substituting

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

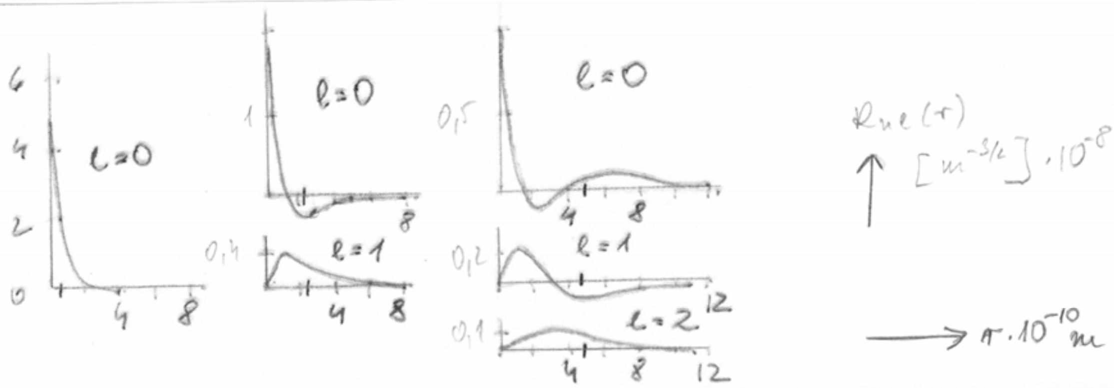
R(r) is the radial part of the wavefunction

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

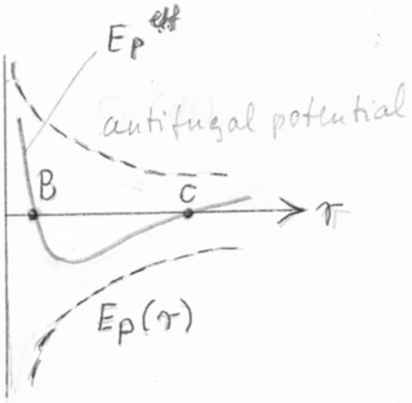
s orbit ℓ = 0 $E_p^{eff} = E_p$ - attractive

Centrifugal potential : repellent

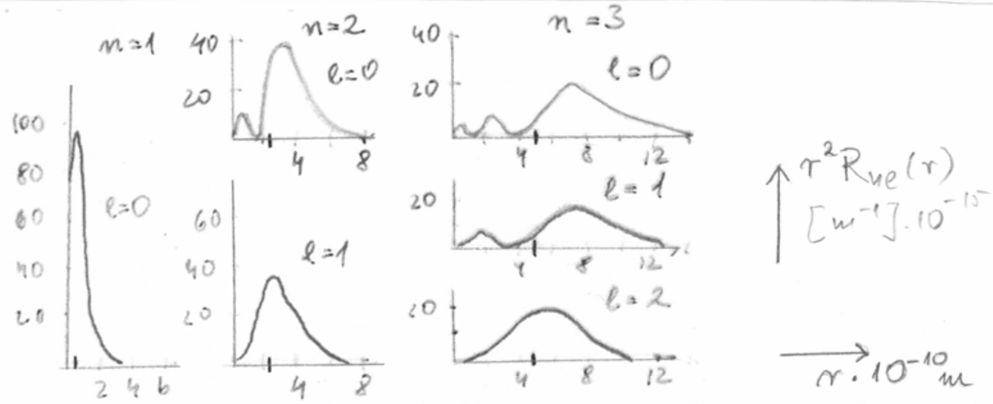
E_p^{eff} for ℓ > 0   sum of the two

→ 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

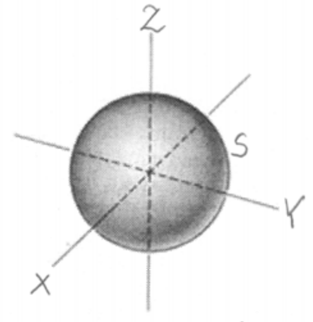
ℓ > 0, p, d electrons : less sensitive

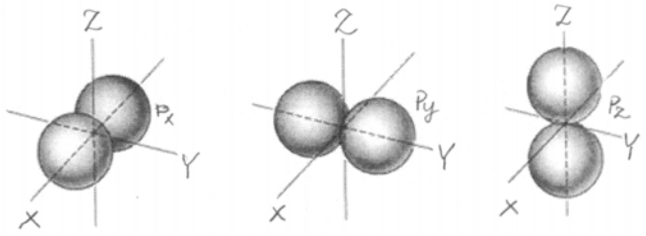
	l	m_l	$Y_{l,\, m_l}$
s	0	0	$Y_{00} = \frac{1}{\sqrt{4\pi}}$
p	1	0	$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$
		±1	$Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\varphi}$
d	2	0	$Y_{20} = \frac{1}{2}\sqrt{\frac{5}{4\pi}}(3\cos^2\theta - 1)$
		±1	$Y_{2\pm1} = \mp\sqrt{\frac{15}{8\pi}}(\sin\theta\cos\theta)e^{\pm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

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

ψ is the superposition of such directional (Y) and R radial distributions

l larger → more complicated





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

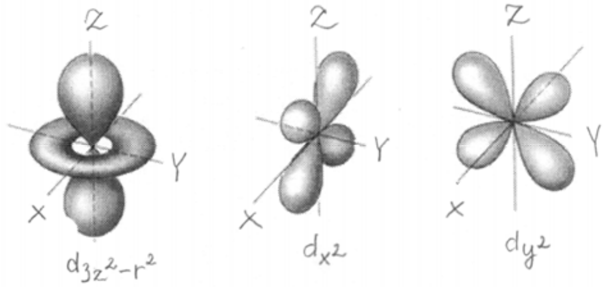
p

Real parts

Eigenfunctions of l, and $|m_l|$

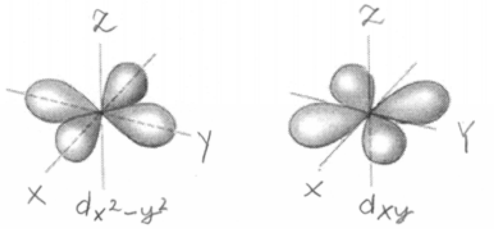
$|m_l| = 1$

$|m_l| = 0$



$d_{3z^2-r^2}$ d_{x^2} d_{y^2}

d



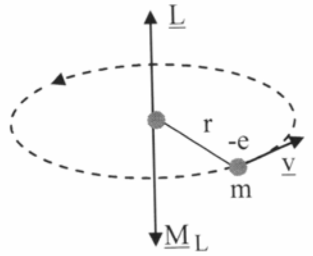
$d_{x^2-y^2}$ d_{xy}

$|m_l| = 2$

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

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

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

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

Due to the negative electron charge:

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

z component of the magnetic moment

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

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

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

Let the z axes be ∥ with $\underline{B}$

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

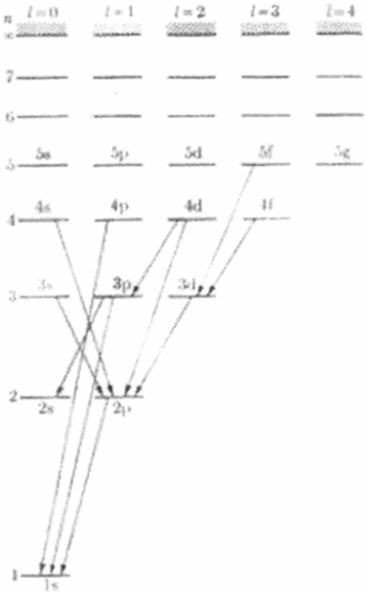
But for an orbital with given l → $2l+1$ different m_e's

⇝ $2l+1$ different discreet E_B values

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

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 $\Delta l = \pm 1$ $\Delta m_l = 0, \pm 1$
because of conservation of angular momentum
Angular momentum of the photon $\equiv 1$
Meta stable states (e.g. 2s) 2s → 1s transition is forbidden (dipole approx.)

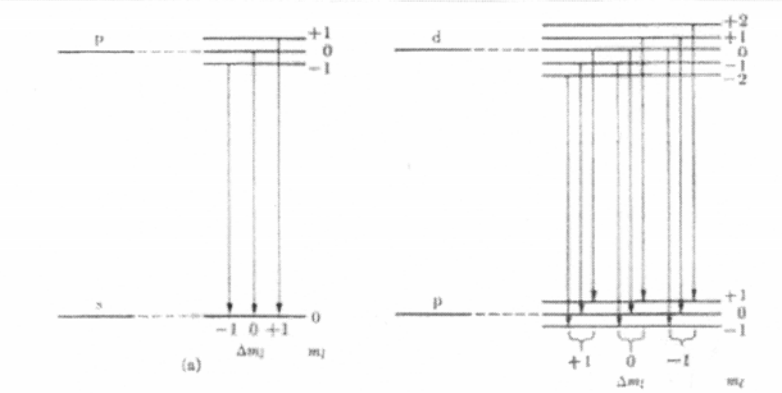
Orbit $\xrightarrow{q.m.}$ Wave function
Schrödinger equation in central force field
Shown earlier: $\psi(r, \theta, \varphi) = R(r) \cdot Y(\theta, \varphi)$
Due to the central symmetry $Y(\theta, \varphi)$ is identical for all central potential, determined by $|\underline{L}|$ and L_z

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

Energy of the electron

$E = E_n + E_B$

$\leadsto$ $\forall$ (n, l) level splits into $(2l+1)$ levels with differe 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

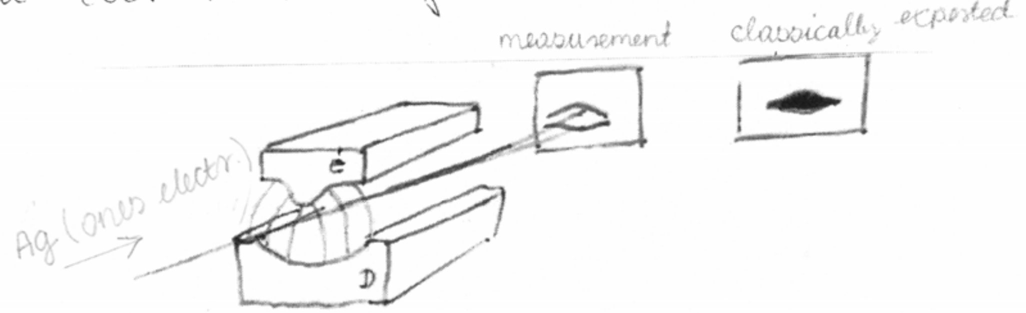
Δm_l can be $0, \pm 1$ only → triplet /3 lines/

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 $\quad \underline{F} = \text{grad}(\underline{M}\cdot\underline{B})$

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

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 $\quad (2s+1) = 2 \;\rightsquigarrow\; s = \frac{1}{2}$

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

$$\left(M_L = \frac{e}{2m_e} L\right)$$

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

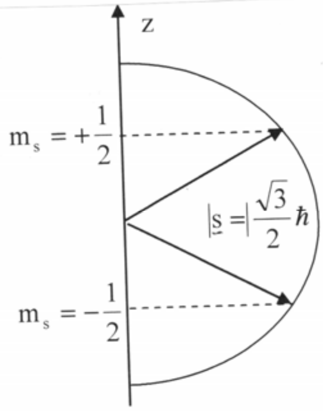
l given $\rightarrow$ $2l+1$ different directions

For the spin

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

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

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



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

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

Spin wavefunctions:

χ_{m_s}

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

$\chi_+ \quad m_s = +\frac{1}{2}$

$\chi_- \quad m_s = -\frac{1}{2}$

So the total wavefunction of an electron in an atom is

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

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)

Microscopic particles in a limited space

Discreet wavefcts. solve the Schr. eq. → discreet energy levels

Ψ, E_n – depend on the potential, boundary conditions

pot. box, $E_n \sim n^2$ 3 dim $\{n_1^2, n_2^2, n_3^2)$

harm osc. $E_n \sim n + \frac{1}{2}$

H atom: Coulomb potential (centrally symm. 3 dim)

$$E_n \sim -\frac{1}{n^2}$$

3 dim $\{n, l, m_l\}$ + spin m_s

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

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

$L_z = \hbar m_l$

$n = 1, 2, 3 ..$

$l = 0, 1 .. (n-1)$

$m_l = 0, \pm 1 .. \pm l$

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

Selection rules $\Delta l = \pm 1$ $\Delta m_l = 0, \pm 1$

Magnetic moment $\underline{M_l} = -\frac{e}{2m_e}\underline{L}$

$$\underline{M_s} = -\frac{e}{m_e}\underline{S}$$

Atoms / I.

Helium atom
The exclusion principle

Atoms with multiple electrons

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

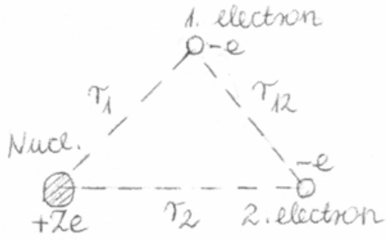
The electrons are not independent → interact

Approximate solutions only

The Helium atom

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

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



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

independent particle model

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

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

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

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

2. approximation: interaction considered as perturbation

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

$$E_{He} = -2\frac{Rhc(Z-S)^2}{1^2}$$

$\downarrow$

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

— The possible electron states

1. Independent particle model

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

$\left.\begin{array}{l}\text{1. electron in state } a\\ \text{2. electron in state } b\end{array}\right\} \rightarrow \psi_{aton} = \psi_a(1)\,\psi_b(2)$

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

2. Shielding potential perturbation

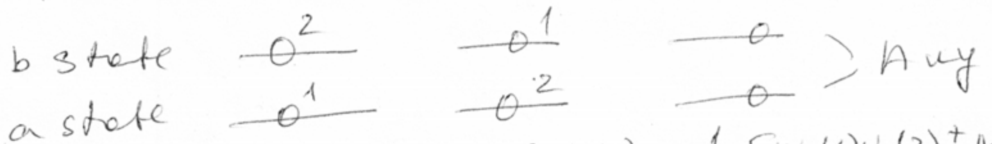
Assumed to be central ↦ $\frac{1}{r}$ changes some ⇝

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

But the electrons are indistinguishable!

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

⇝ ψ_{atom} must reflect this symetry, i.e. $|\psi_{atom}|^2$ must not change when exchanging electron 1⇔2



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

The symetry requirement is fulfilled by the states

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

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

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

The energies of the symmetric and antisymmetric 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.

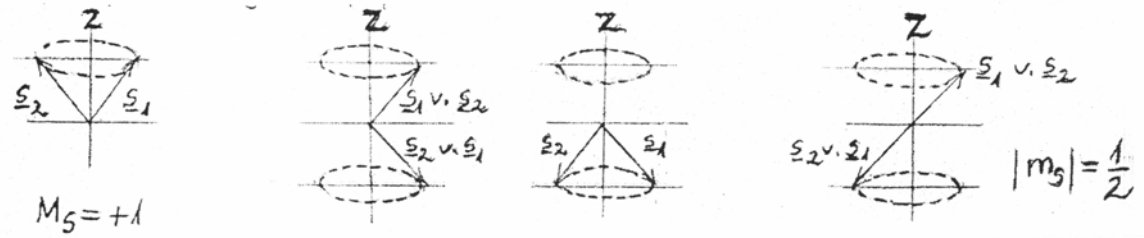
$\rightsquigarrow$ Sets of 2 stationary states and energy level systems
(except when $a = b \rightsquigarrow \psi_A = 0$, only $\psi_S\ \exists$.)

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

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

triplet $M_S = +1, 0, -1$
$(2S+1) = 3$

singlet $M_S = 0$
$(2S+1) = 1$



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

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

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 energi

ψ_S (orbit) always singlet → χ_A is attached

ψ_A (orbit) always triplet → χ_S — " —

Therefore:

The total wavefunction of the system of electrons is always antisymmetric

He: S = 0 parahelium /with singlet states/

S = 1 ortohelium /with triplet 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

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12} \qquad \hat{H}_1 = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1}$$

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

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

$i = 1,2$

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

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

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

where $\psi = \psi_A$ or ψ_S

Using the above:

The energy

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

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

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

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

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

$K > 0$

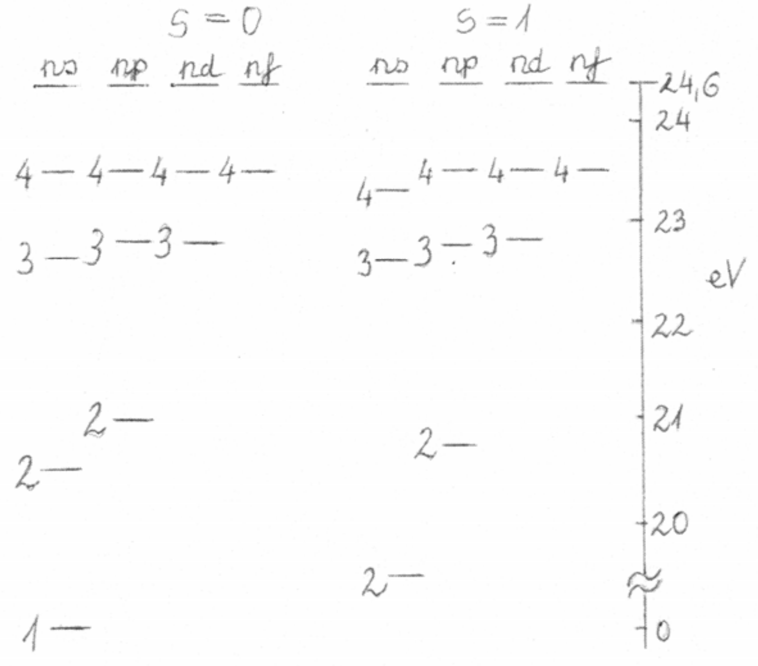
$K \rightarrow$ —— " —— $\varrho_1' = -e\psi_a^*(1)\psi_b(1)$ and $\varrho_2' = -e\psi_b^*\psi_c$

charge distributions

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

$\rightsquigarrow$ For ψ_S /singlet/ $+K$ higher
ψ_A /triplet/ $-K$ lower $\Big\} \rightsquigarrow$

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



(1 of the electrons in the 1s state)

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

Microscopic particles in a limited space
Discreet wavefcts. solve the Schr. eq. → discreet energy levels

Ψ, E_n – depend on the potential, boundary conditions
pot. box , $E_n \sim n^2$ 3 dim $\{n_1^2, n_2^2, n_3^2)$
harm osc. $E_n \sim n + \frac{1}{2}$

H atom : Coulomb potential (centrally symm. 3 dim)

$E_n \sim -\frac{1}{n^2}$

3 dim $\{n, l, m_l\}$ + spin m_s

$$\Psi = \underset{n,l}{R}(r)\, Y_{l m_l}(\theta, \varphi)\, \chi_{m_s}$$

$L^2 = \hbar^2 l(l+1)$
$L_z = \hbar m_l$
$n = 1, 2, 3 ..$
$l = 0, 1 .. (n-1)$
$m_l = 0, \pm 1 .. \pm l$
$m_s = \pm \frac{1}{2}$

Selection rules $\Delta l = \pm 1$ $\Delta m_l = 0, \pm 1$

Magnetic moment $\underline{M_l} = -\frac{e}{2m_e}\underline{L}$

$$\underline{M_s} = -\frac{e}{m_e}\underline{S}$$

He atom 2 electrons (indistinguidable)

$$\Psi = \frac{1}{\sqrt{2}}\left[\Psi_a(1)\Psi_b(2) \pm \Psi_a(2)\Psi_b(1)\right] \cdot \begin{cases} \chi_A \\ \chi_S \end{cases}$$

total Ψ always antisymmetric

The exclusion principle

Atom with multiple electrons

Each electron charactenied 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

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

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

2 electrons with identical sets of quantum numbers

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

Conclusions: 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

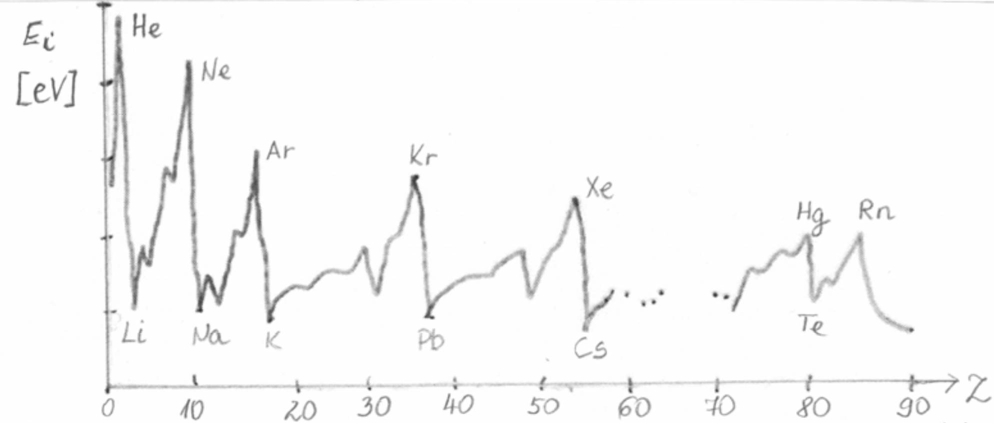
Electron structure of atoms

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 $1s^2$

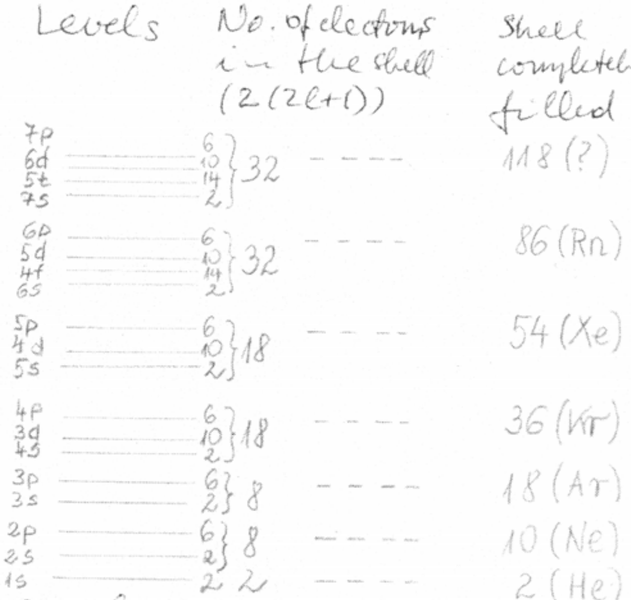
Let us build up the atoms of the elements from $Z=1$

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



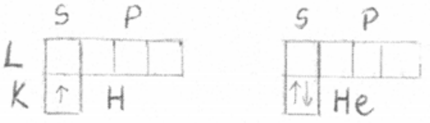
Full shells:

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

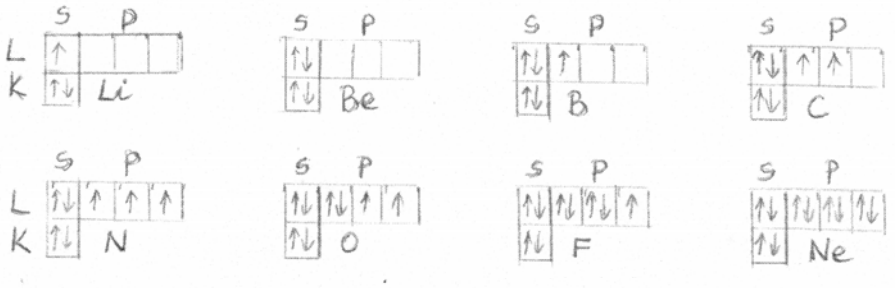
noble gases

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

Build up of the first 10 elements



$n = 1, 2, 3, 4 \ldots$
K L M N…



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

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

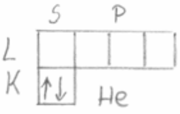
$l=1 \rightarrow p \qquad m_l = +1, 0, -1, \; m_s = \pm \frac{1}{2}$

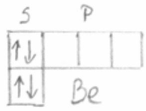
In the course of filling the shells:

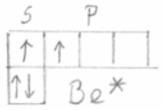
maximum number of parallel spins

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





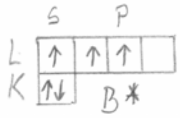


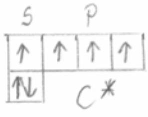
He and Be: completely filled 1s and 2s levels

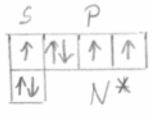
He – noble gas Be – is not

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





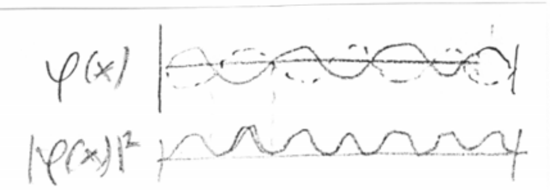


Physical and chemical properties of atoms are determined by the ~~ground~~ electron configurations of the ground state and the closely lying excited states.

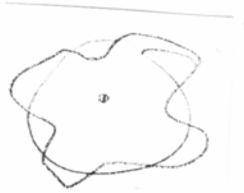
E.g.: noble gases: filled shells
large energy difference to the next unfilled energy state.

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

Time dependent Schrödinger equation



Standing wave oscillates



De Broglie

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

$$\varphi=\varphi(x)=Ae^{ikx}$$

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

$$\Psi(x,t)=\varphi(x)e^{i\omega t}=Ae^{i(kx-\omega t)}$$

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

$$\omega=\frac{E}{\hbar}$$

oscillation frequency

Time dependent Schr. eq.

$$i\hbar\varphi(x)i\omega e^{-i\omega t}=+\hbar\frac{E}{\hbar}\varphi e^{i\omega t}=E\cdot\varphi e^{i\omega t}$$

$$=+\hbar\frac{E}{\hbar}\cdot\varphi(x)e^{i\omega t}=$$

$$=E\cdot\varphi(x)e^{i\omega t}$$

Phase velocity

$$V_{ph}=\frac{\omega}{k}$$

Time dependent wavefct.

$$\psi(x,t) = C\, e^{\frac{i}{\hbar} p_x x - \frac{i}{\hbar} E t} = C\, e^{i k_x x - i \omega t}$$

$$k_x = \frac{p_x}{\hbar} \qquad \omega = \frac{E}{\hbar}$$

$\lambda_d \rightarrow$ De Broglie wavelength $= \frac{2\pi}{k_x} = \frac{h}{p_x} = \frac{\hbar}{\sqrt{2mE}}$

Electron with 1eV kinetic energy $\lambda_D = 1{,}23\,\text{nm}$

$(1{,}6 \cdot 10^{-19}\,J)$ $m_e = 9 \cdot 10^{-31}\,kg$

$h = 6{,}6 \cdot 10^{-34}\,J\,sec$

Photon

$$\lambda_{ph} = \frac{c}{\nu} = \frac{hc}{E}$$

Photon with 1eV energy $\lambda_{ph} = 1{,}24\,\mu m$

Resolution electron microscope

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

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

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.

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

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

E.g.

– Particle moving to direction +x : $\varphi(x)=A\,e^{ikx}$ ⇝

$$\varphi(x,t)=\varphi(x)\,e^{iEt/\hbar}=A\,e^{i(kx-\omega t)}$$

≡ 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 these 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 $\omega = (E_1 - E_2)/\hbar \rightsquigarrow$ emission or absorption of electromagnetic wave

$E_1 - E_2 = h\nu \Rightarrow$ 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

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

$K \neq 0$ $\quad \psi = \sum_r c_r(t)\varphi_r e^{-\frac{i}{\hbar}E_r t}$ 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

$$\frac{dc_k}{dt} = -\frac{i}{\hbar}\sum_r K_{kr} c_r e^{i\omega_{kr}t}$$

$K_r = \int \varphi_k K(t)\varphi_r \, dx$

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

Solution: with successive approximation

e.g. electromagnetic dipole interact. $K = -e\underline{\mathcal{E}}\cdot\underline{X}$

n th approximation

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

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

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

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

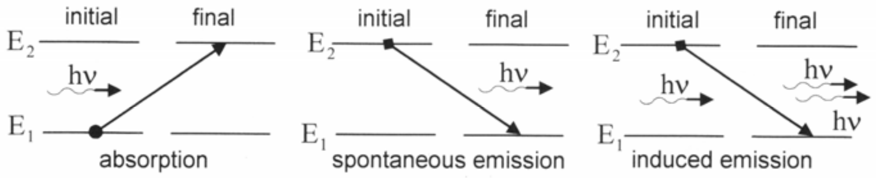
Higher order transitions → smaller probabilities

- 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

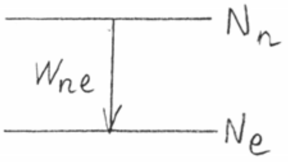


Lifetime of excited state $\sim 1/W(g \to \sum_i)$ all permitted transitions

atoms, molecules $\sim 10^{-8}$ sec

nuclei: $\sim 10^{-8} - 10^{-4}$ sec

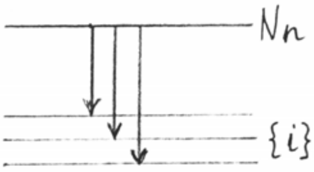
$\tau_u = \frac{1}{W_{ne}}$ radiative lifetime



$$\frac{dN_n}{dt} = -W_{ne}N_n \rightsquigarrow N_n = N_n^{(0)} e^{-W_{ne}\cdot t} =$$

$$= N_n^{(0)} e^{-\frac{t}{\tau_n}}$$

$$\frac{dN_n}{dt} = -\underbrace{\left(\sum_i W_{ni}\right)}_{\frac{1}{\tau_n} = W_n} N_n$$



Nonradiative decay – collisional decay

$$W_{ne} = W_{ne}^{rad} + W_{ne}^{coll.}$$

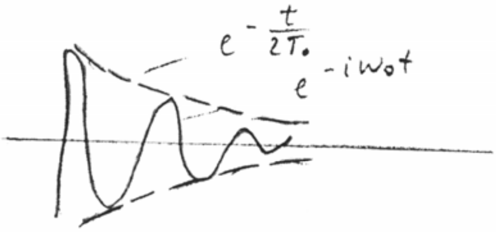
$$\tau_n = \frac{1}{W_n} = \frac{1}{W_n^{rad} + W_n^{coll}}$$

- Collisional lifetimes

gases ~ (radiation lifetime : pressure in low)
liquids / solids : for external electrons
phonon or lattice relaxations
$10^{-12} - 10^{-13}$
for inner shell electrons
schielding → no coll. broadening

- Emission broadening and linewidth
Finite length more:

$$E(t) = E_0 e^{-\frac{t}{2\tau_0}} e^{-i\omega_0 t} \qquad \begin{matrix} t \geq 0 \\ t < 0 \end{matrix}$$

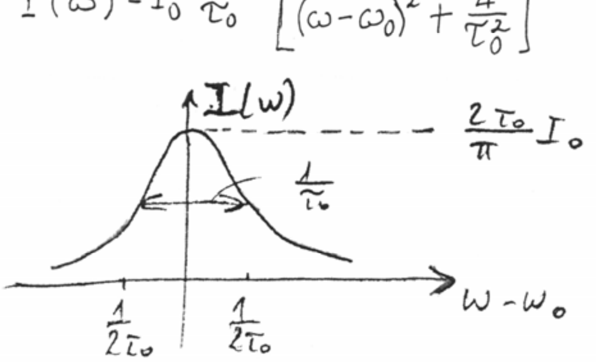


$$\text{F.T.} \quad E(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} E(t) e^{i\omega t} dt =$$

$$= \frac{E_b}{\sqrt{2\pi}} \int_0^{\infty} e^{i\left[(\omega-\omega_0)+\frac{i}{2\tau_0}\right]} dt$$

$$= -\frac{E}{\sqrt{2\pi}} \frac{1}{i\left[(\omega-\omega_0)+\frac{i}{2\tau_0}\right]}$$

$$I(\omega) = I_0 \frac{2\pi}{\tau_0} \frac{1}{\left[(\omega-\omega_0)^2 + \frac{4}{\tau_0^2}\right]} \qquad I_0 = \int_0^{\infty} I(\omega) d\omega$$



Lorentzian distribution
$$\Delta W^{FWHM} = \frac{1}{\tau_0} = 2\pi \Delta\nu$$
↓
linewidth

natural + collisional ← homogenous broadening

Doppler broadening in gases

Light emitted with ν_0 freq., for a period Δt

Emitter moves with velocity v (towards observer)

During Δt $c\Delta t$ distance changes to $(c-v)\Delta t$

→ λ is compressed → $\lambda\nu = c$ → ν increases

$$\nu = \frac{c\,\Delta t}{(c-v)\,\Delta t}\,\nu_0 = \left(\frac{1}{1-\frac{v}{c}}\right)\nu_0 \approx \left[1+\frac{v}{c}+\left(\frac{v}{c}\right)^2+\dots\right]\nu_0$$

moving away

$$\nu \approx \left[1-\frac{v}{c}+\left(\frac{v}{c}\right)^2-\right]\nu_0$$

In gases → atoms molecules thermal motion

$$\bar{v} = \sqrt{\frac{8\pi kT}{M\pi}}$$

Boltzmann dist..

$$P(v_x) = \left(\frac{M}{2\pi kT}\right)^{1/2} \exp\left\{-\frac{M}{2kT}v_x^2\right\}dv_x$$

Gaussian shape

x → direction of observation

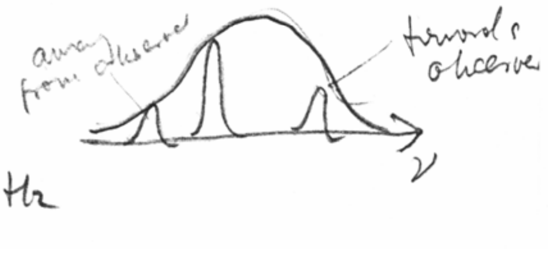
$$\nu = \nu_0\left(1+\frac{v_x}{c}\right)$$

Probability $g(\nu)\,d\nu$ that the transition frequency is between ν and $\nu+d\nu$ → v_x in between $v_x = (\nu-\nu_0)\frac{c}{\nu_0}$ and $v_x + dv_x = (\nu+d\nu-\nu_0)\frac{c}{\nu_0}$

$$g(\nu)\,d\nu \sim \exp\left\{-\frac{M}{2kT}\frac{c^2}{\nu_0^2}(\nu-\nu_0)^2\right\}$$

$$I(\nu) = \left(\frac{M}{2\pi kT}\right)^{1/2}\left(\frac{c}{\nu_0}\right)I_0 \exp\left\{-\frac{M}{2kT}\frac{c^2}{\nu_0^2}(\nu-\nu_0)^2\right\}$$

Inhomogeneous broadening



FWHM

$$\Delta\nu_D = 2\nu_0\sqrt{\frac{2(\ln 2)kT}{Mc^2}} \sim 10^9\,\mathrm{Hz}$$

Molecules/I.

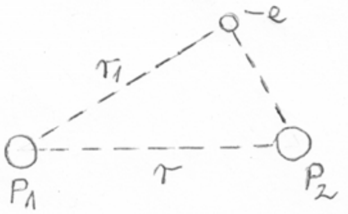
H_2^+, bonding and anti-bonding molecular orbitals

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

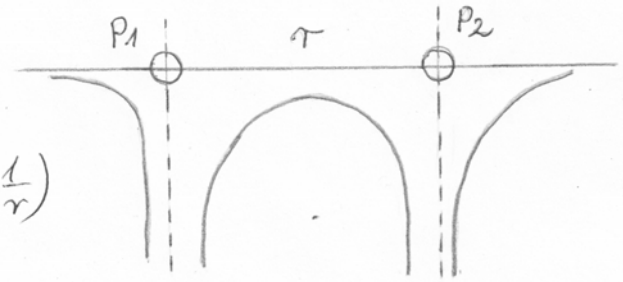


2p + 1e $H + H^+ = H_2^+$

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

Stationary states:

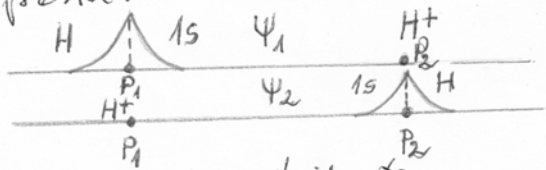
Schrödinger equation



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

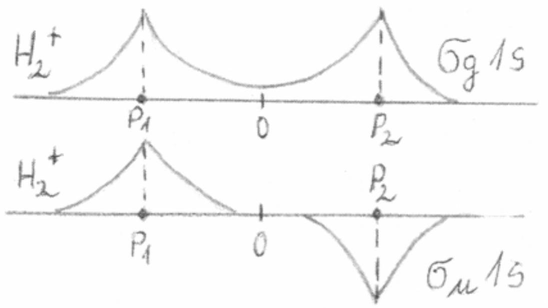


el. around p_1: 1s H atom, p_2 free

el. around p_2: 1s H atom, p_1 free

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

Ψ_{el} must follow the symmetry of the potential

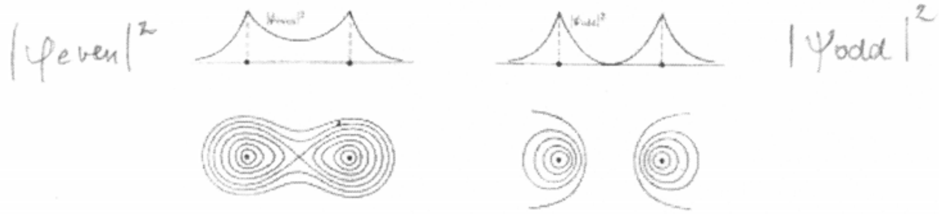


$\psi_{even} \approx \psi_1 + \psi_2 = \sigma_g 1s$

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

Generation of molecular orbitals by linear combination of atomic orbitals

The probability distribution $|\psi|^2$



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

⇝ $\sigma_g 1s$ 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

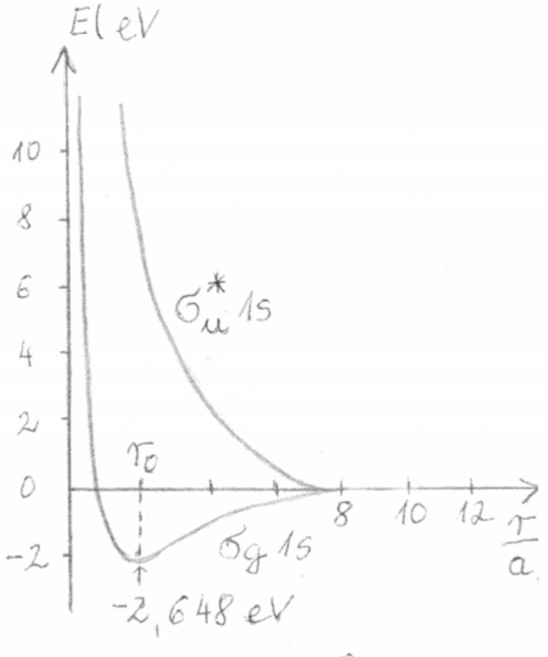
$r = r_0 \mapsto$ minimum in potential energy for $\sigma_g 1s$

↓

Stable H_2^+ configuration

⇝ $\sigma_g 1s$ bonding wavefunction

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



$r_0 = 1,06$ Å

The energy of these states:

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

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

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

B and S are quantum-mechanical term

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

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

No overlap $B = S = 0$

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

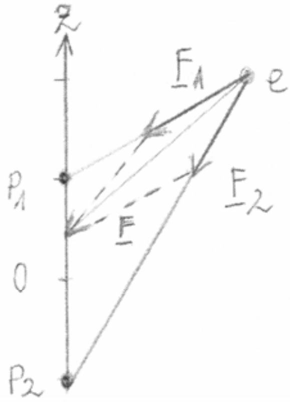
– no minima

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

Molecular orbital of diatomic molecules

$H_2 \rightarrow 2$ electrons

Exclusion principle ! : spin plays a role beside orbitals



the force is not centrally but axially symmetric
⇝ $\underline{L}$ is not constant of motion

Since the force 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	±3...	
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 : $\lambda n l$

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

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.

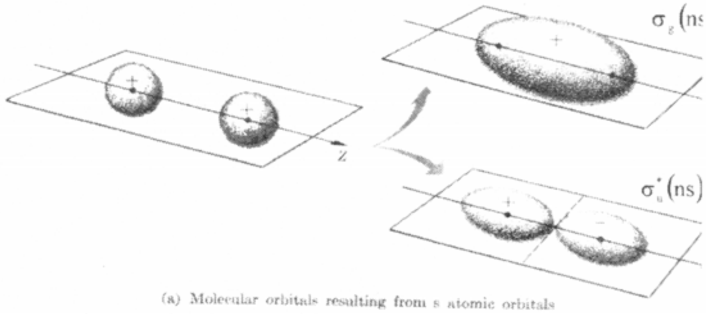
Chemical bond: approaching two atoms

$\psi_1 \pm \psi_2$

Angular distributions:

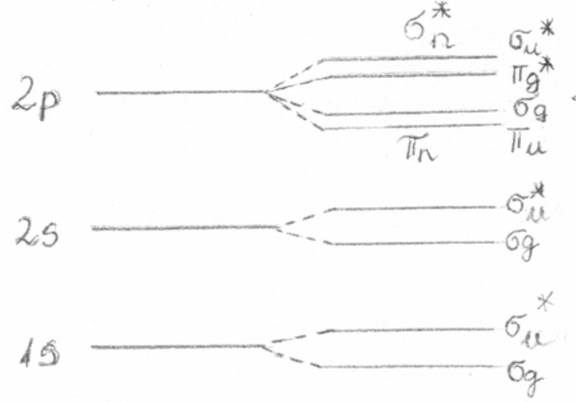
nodal planes ----

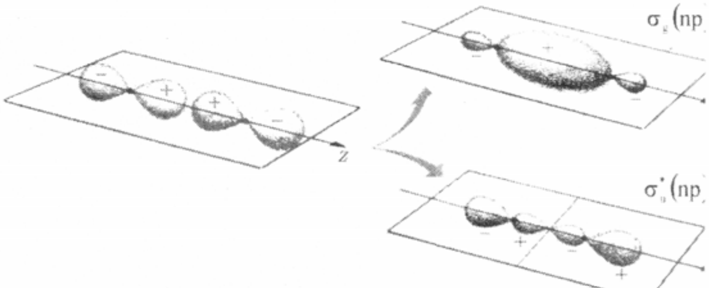
antibonding states(*)



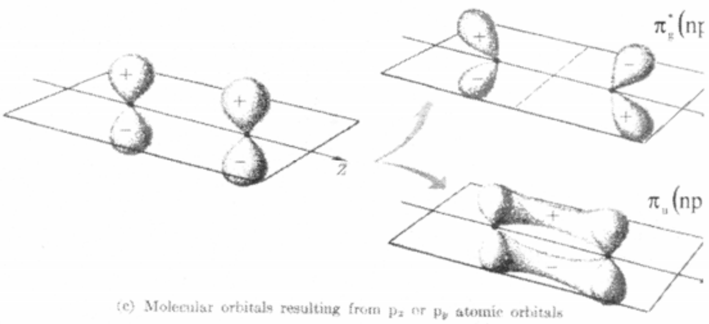
(a) Molecular orbitals resulting from s atomic orbitals

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

$H_2 \rightarrow 2p + 2e$

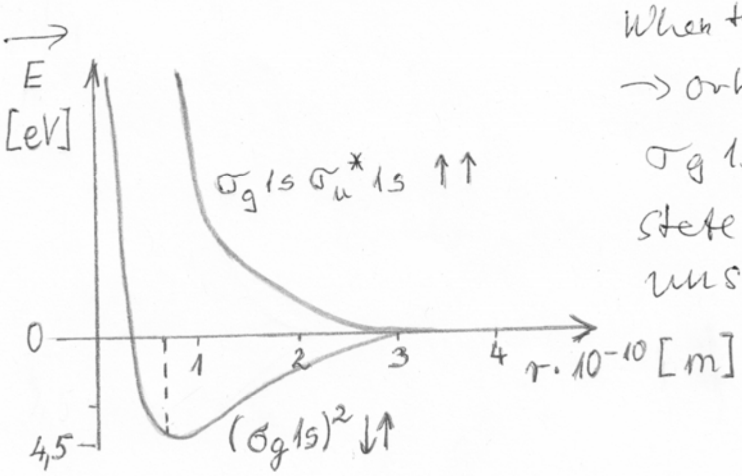
$$E_p = \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_1} - \frac{1}{r_1'} - \frac{1}{r_2} - \frac{1}{r_2'} + \frac{1}{r_{12}} + \frac{1}{r}\right)$$

One can not tell which electron belongs to which proton

Exclusion principle ; spin must be taken into account

$\rightarrow$ 2 electrons on $\sigma_g 1s$ bonding state $\rightarrow \uparrow\downarrow$ spins

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



When the two spins are $\uparrow\uparrow$

$\rightarrow$ orbital must be antisymmetric

$\sigma_g 1s\, \sigma_u^* 1s$ $\rightarrow$ the antibonding state dominates

unstable

He_2^+ molecule

3 electrons

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

Total orbital angular momentum $M_L \hbar$

$M_L = \sum_i m_{l i}$

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

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

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

Electron configuration of homonuclear diatomic molecules

	$\sigma_g 1s$	$\sigma_u^* 1s$	$\sigma_g 2s$	$\sigma_u^* 2s$	$\pi_u 2p$	$\sigma_g 2p$	$\pi_g^* 2p$	$\sigma_u^* 2p$	Diss. energy
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 center of symmetry!

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

Electrons on the unfilled shells participate in the bond out

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

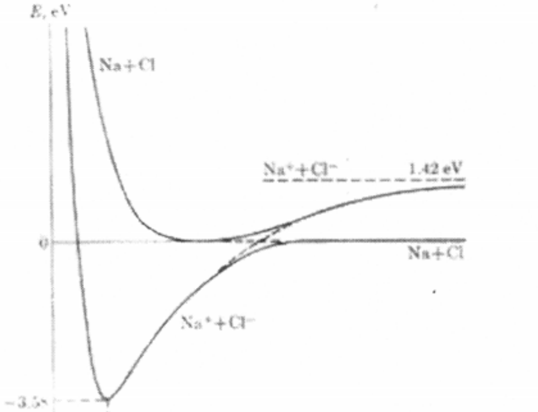
polarization → electric dipole moment : $3 \cdot 10^{-29}$ Cm

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 ⟼ <u>ionic bond</u>



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

Molecules

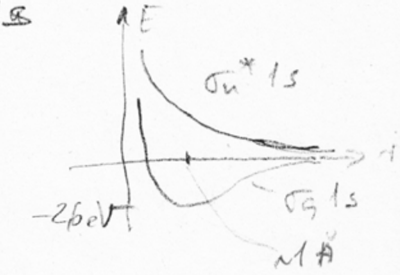
Valence electrons in non-central symmetric potential

H_2^+ $\Psi_1 = 1s$ $\Psi_2 = 1s$ Combination of atomic orbitals

Symmetry : $1 \Longleftrightarrow 2$

$\Psi_{even} = \Psi_1 + \Psi_2$ $\Psi_{odd} = \Psi_1 - \Psi_2$

Covalent bond



$$E = E_a + \frac{e^2}{4\pi\varepsilon_0 r} - \frac{A \pm B}{1 \pm S} \quad \begin{matrix} + & \Psi_g \\ - & \Psi_u \end{matrix}$$

A, B, S → overlap of Ψ_1 and Ψ_2

σ, π, δ .. $|m_\ell| = 0, 1, 2 \ldots$

Molecular orbital wavefunctions: — Figure

Exclusion principle $(\sigma_g 1s)^2$ ↑↓ – stable

$\sigma_g 1s \; \sigma_u^* 1s$ ↑↑ – unstable

. Pauli principle dynamics : electric attraction vs. extend excitation

Covalent bond for diatomic molecules with multiple electrons

Stability: ratio of bonding/antibonding orbitals

Heteronuclear molecules: → ionic bond

Multiatomic molecules

Interesting: geometrical arrangement /symmetry/

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

E.g. H_2O

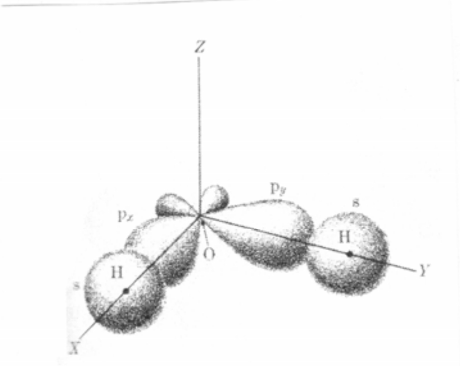
oxygen

	s	p		
L	↑↓	↑↓	↑	↑
K	↑↓			

2 electrons ↑↑ spins must have different orbitals: p_x, p_y

the two hydrogens: 1s electrons

Maximal overlap



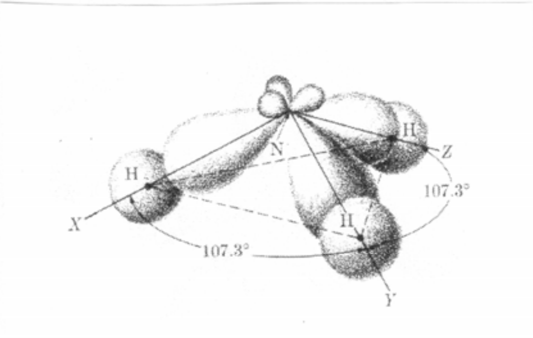
The p orbitals of the el-s of oxygen are distorted because of the H atoms
→ dipole moment
Angle > 90° (= 104,5°), because H atoms repel each other

NH$_3$

nitrogen

	s	p		
L	↑↓	↑	↑	↑
K	↑↓			

3 uncompensated spin p electron
p_x, p_y, p_z
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 CH_4?

Hybridization

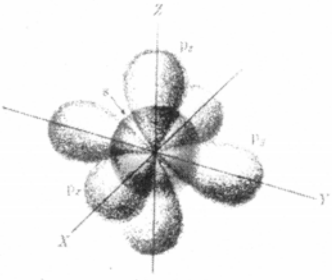
4 equivalent wavefunctions from linear combination of s, p_x, p_y, and p_z → sp^3 hybridization

$$\psi_1 = \frac{1}{2}\left(s + p_x + p_y + p_z\right)$$

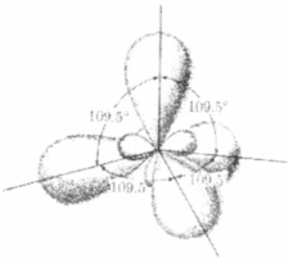
$$\psi_2 = \frac{1}{2}\left(s + p_x - p_y - p_z\right)$$

$$\psi_3 = \frac{1}{2}\left(s - p_x + p_y - p_z\right)$$

$$\psi_4 = \frac{1}{2}\left(s - p_x - p_y + p_z\right)$$



(a) s, p_x, p_y, and p_z wave functions

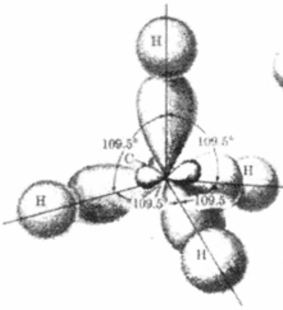


(b) sp^3 hybridized wave functions

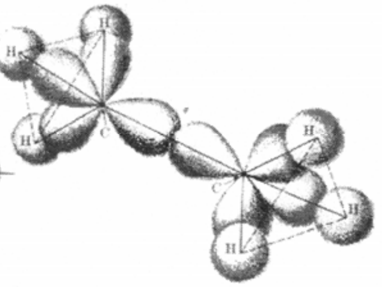
ψ_i → not eigenfunctions of angular momentum.

sp^3 hybridization describes

CH_4 methane C_2H_6 ethane



(a)



(b)

Ethane $H_3C - CH_3$

↓

C−C bond with overlap of two sp^3 hybrids: σ bond

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

sp^2 hybridization

s, p_x, p_y hybridizes + p_z

$$\left.\begin{aligned}\Psi_1 &= \frac{1}{\sqrt{3}}\left(s+\sqrt{2}\,p_x\right)\\ \Psi_2 &= \frac{1}{\sqrt{3}}\left(s-\frac{1}{\sqrt{2}}p_x+\sqrt{\frac{3}{2}}\,p_y\right)\\ \Psi_3 &= \frac{1}{\sqrt{3}}\left(s-\frac{1}{\sqrt{2}}p_x-\sqrt{\frac{3}{2}}\,p_y\right)\end{aligned}\right\}\text{ In the x, y plane at } 120^\circ$$

$$\Psi_4 = p_z$$

Ethylene : C_2H_4

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

σ π bond

σ between two sp^2

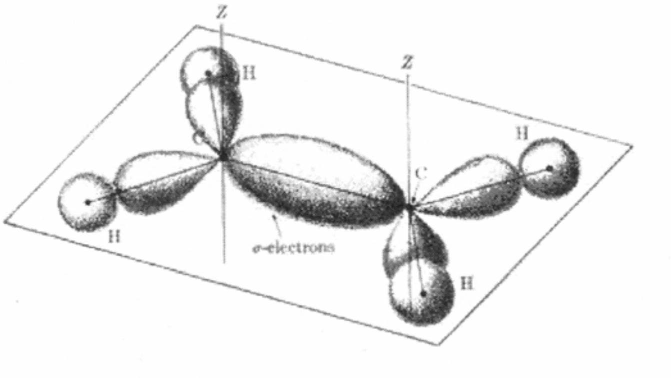
π between two p_z

π : weaker than σ

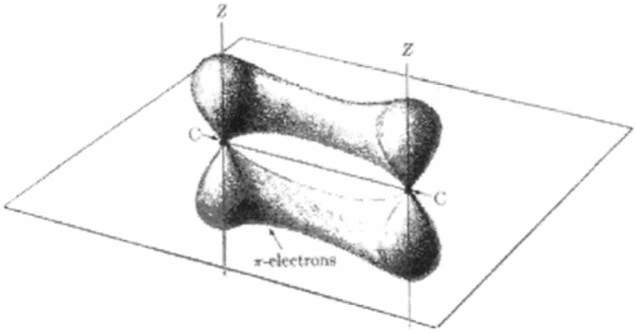
σ π bond : stiff

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

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

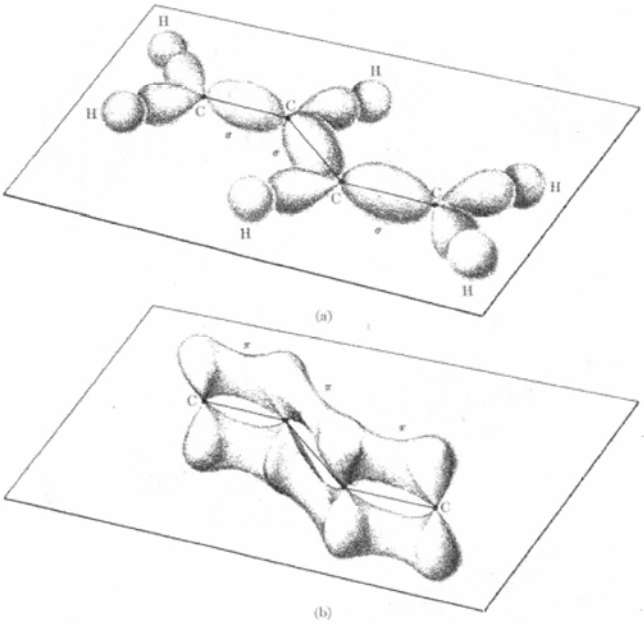
σ 2π bond

σ between two sp hybrids

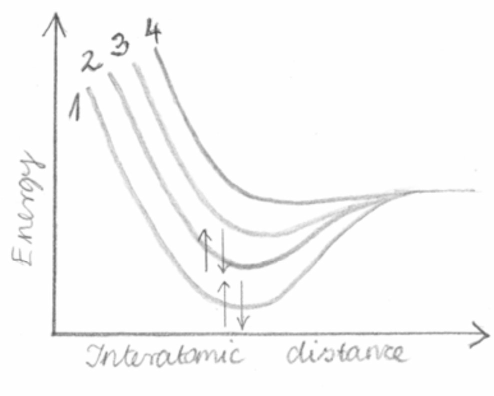
π between p_x - s and

p_y - s

Conjugated molecules e.g. C_4H_6 butadiene



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
Those electrons are not localized, they move freely along the chain
Their wavefunction: with combination of atomic orbitals



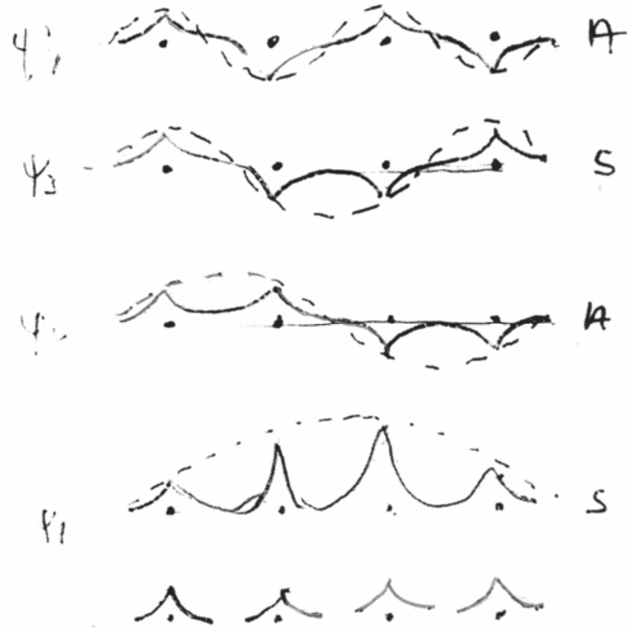
4 wavefunctions
4 energy levels
but only 2 are filled,
2 are empty ⇝
absorption in the visible
↓
colour

Polyene chain molecules consist of 2n C atoms are similar

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

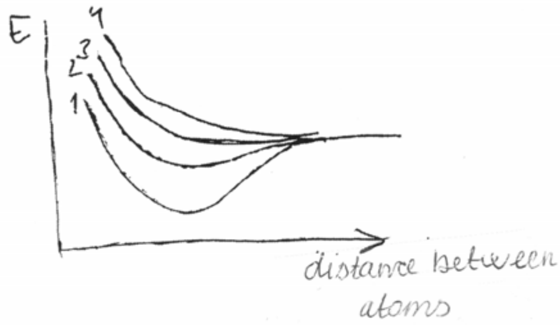
$2n\pi$ electrons, 2n energy levels with 4n electron states.

Conjugated molecules non-localised electrons



C_4H_6 Butadiene

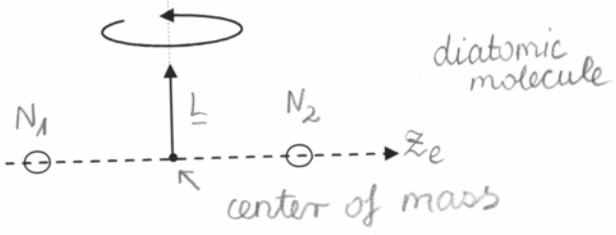
← orbitals by
linear combination
of atomic orbitals
LCAO



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

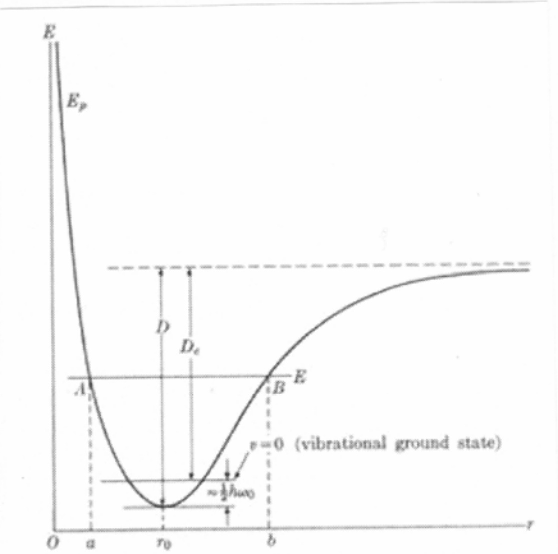
Quantification $L^2 = \hbar^2\, l(l+1)$

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

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

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

Vibration



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

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

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

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

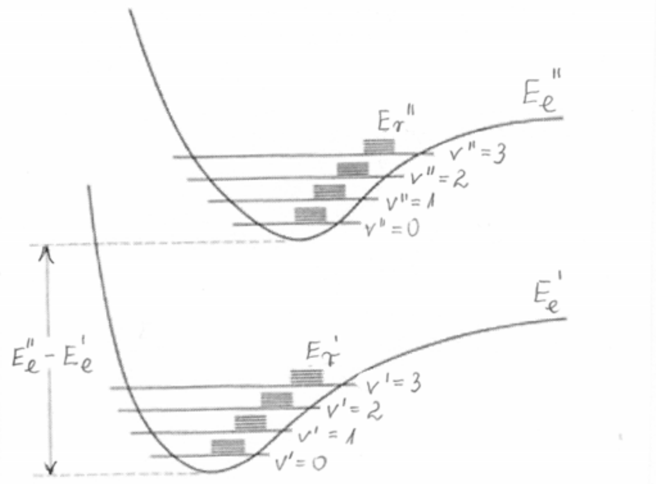
(D = disociation energy)

The full energy:

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

$E_e \rightarrow$ energy of the electron state

$E = E_e + E_v + E_r$



Transitions

Bands in the electronic transitions

Selection rules

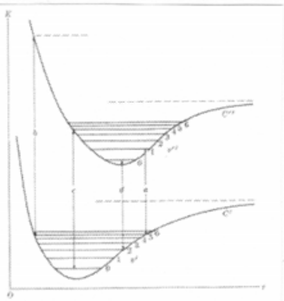
$\Delta l = 0, \pm 1$

$\Delta s = 0$

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.

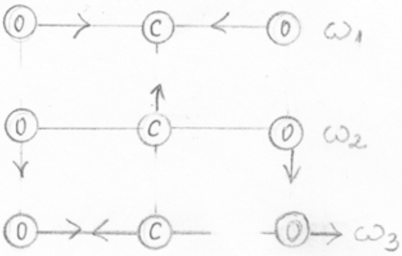


Vibration of multiatomic molecules

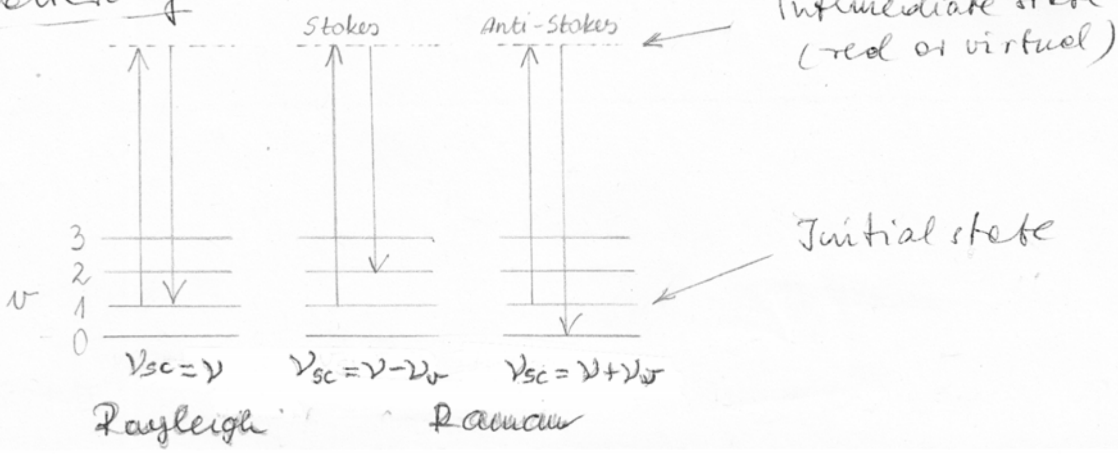
Normal modes (i) e.g. CO_2

combinations $\{v_i\}$

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

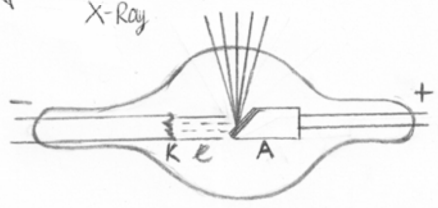


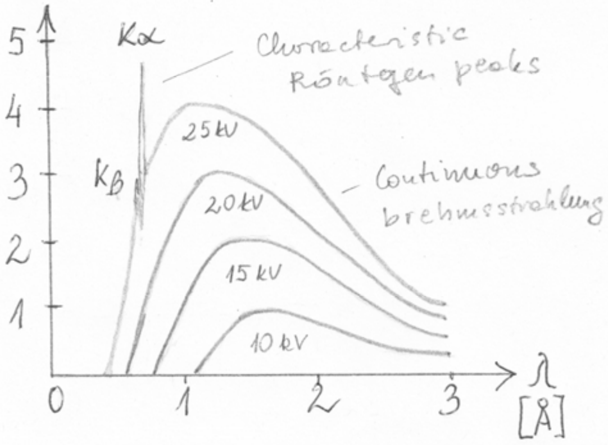
Rayleigh and Raman scattering



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 > 20,1 kV

Sharp peaks: λ peak depends on the anode material

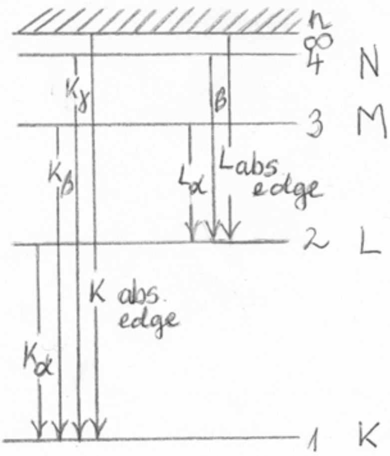
Accelerated electron collides with the atoms of the electrode

knicks 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 knicked 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

Statistical physics

Classical stat. phys.
Maxwell - Boltzmann distribution

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

Statistical equilibrium

N particles $E_1, E_2 \ldots$ 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 $E_i \to E_i + E_{i\,ave} \; (= \varepsilon_i)$

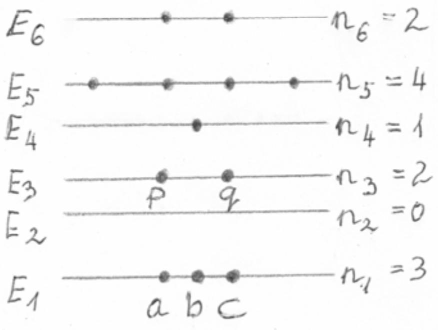
Closed system: U = const, but due to the interaction (e.g. collision) of particles the individual particles change their states ⇝ $\{n_1, n_2, \ldots\} = \{n_i\}$ distribution changes
∃ a distribution with highest probability
$\{n_i\}_p$ ≡ corresponds to the statistical equilibrium
We search for $\{n_i\}_p$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

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

Maxwell - Boltzmann distribution

System of identical and indistinguishable particles

First: assume distinguishability



Assumptions:

1. Probability of filling ∀ energy state is identical
2. Probability of an $\{n_i\}$ distribution is proportional to the number of its realisation 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)

From the N particles we can select n_1 particles to the E_1 state in

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

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

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

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

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

ways.

According to 2. P = probability of the $\{n_i\}$ distribution

When assumpt. 1. ↓: probability of getting to E_i is g_i

(g_i ≡ degree of degeneracy of E_i)

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

— Now when the particles are indistinguishable

→ N! permutation gives the same distribution

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

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

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

$$\ln P = n_1 \ln g_1 + n_2 \ln \quad \dots - \ln n_1! - \ln n_2! \dots$$

Stirlings' form $\quad \ln x! = x \ln x \quad$ when x is large

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

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

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

Differentiating

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

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

$g_i = \text{const.}$

$$\swarrow$$

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

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

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: $\sum_i dn_i = 0$

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

Tour- Lagrange undetemined multipliers α, β

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

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

Statistical physics

no restriction on n_i

N indistinguishable particles, E_i, g_i

$N = \sum_i n_i$ = const $U = \sum_i n_i E_i$ = const. /closed system/

$\{n_i\}$ distribution

$\downarrow$

$\{n_i\}_p$ most probable distribution → thermal equilibrium (statistical)

$P\{n_i\}$ = probability of $\{n_i\}$ ~ the number of realization possibilities

P – combinatorial calc.

$P_{max} \to dP = 0$ with these conditions α, β

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

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

$n_i = \frac{N}{Z} g_i e^{-\beta E_i}$ Maxwell-Boltzmann distr.

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

The most probable distribution (stat. equilibr.)

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

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

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

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

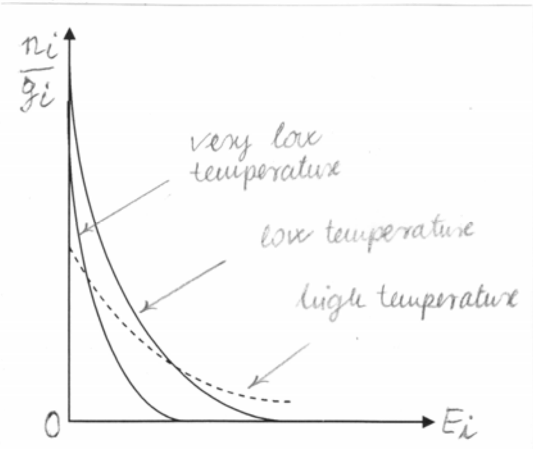
$$F_{ave} = \frac{1}{N}\sum_i n_i F(E_i) \overset{\text{in stat. equil.}}{=} \frac{1}{Z}\sum_i g_i F(E_i) e^{-\beta E_i}$$

What is β?

Def. $\beta = \frac{1}{kT}$ $\quad k = 1{,}38\cdot 10^{-23}$ 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

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

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

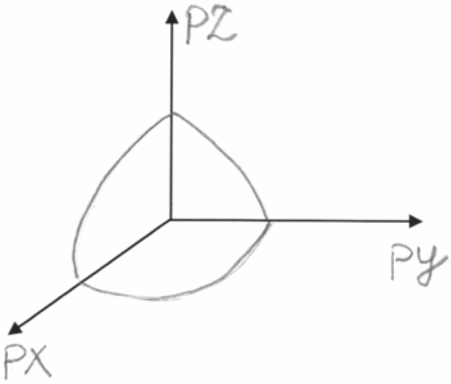
$$= -\frac{N}{Z}\frac{dZ}{d\beta} = -N\frac{d}{d\beta}(\ln Z) \quad \text{but} \quad d\beta = -\frac{dT}{kT^2} \rightsquigarrow$$

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

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)

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



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

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

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

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

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

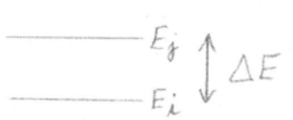
$\downarrow$

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

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

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

E.g. population of the energy levels



$$\frac{n_j}{n_i} = \frac{g_j}{g_i} e^{-\frac{E_j - E_i}{kT}} = \frac{g_j}{g_i} e^{-\frac{\Delta E}{kT}}$$

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. <u>ideal gas</u> /one-atomic molecules, kinetic energy only/

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

$g(E)dE$ number of molecular states between E and $E + dE$

(different velocities $\underline{v}$)

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

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

The distribution instead of n_i

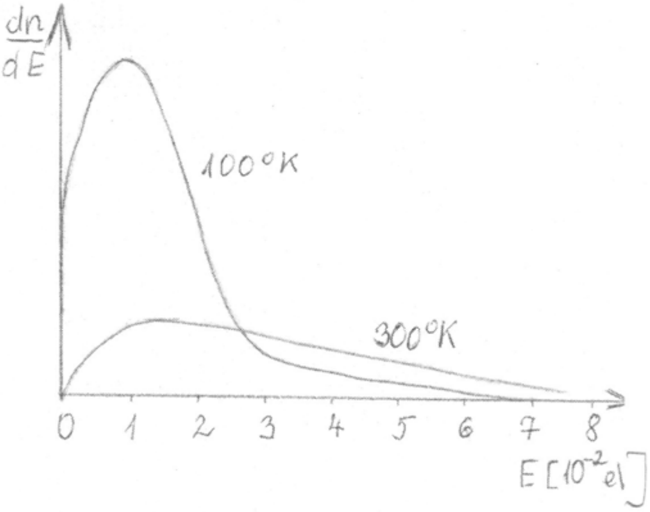
$$dn = \frac{N}{Z} e^{-\frac{E}{kT}} g(E) dE$$

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

(independent of mass!)

Distribution by velocity

$$\frac{dn}{dv} = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \; e^{-\frac{mv^2}{2kT}}$$



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:

$\forall$ distribution is equivalent with Maxwell-Boltzmann

Statistical physics II.

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

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 $\uparrow$ ~> antisymmetric wavefunction
→ Fermi-Dirac stat. fermions

2. Exclusion principle $\downarrow$ ~> 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~~s~~ 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 a $\{n_i\}$ distribution

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

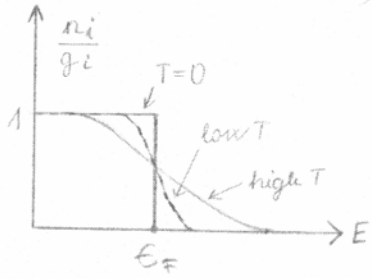
Most probable distribution (stat. equilibr.) → P_{max}

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

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

Def.: $\alpha = -\frac{\epsilon_F}{kT}$ $\qquad \epsilon_F$ = 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 $(n_i = 0)$

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

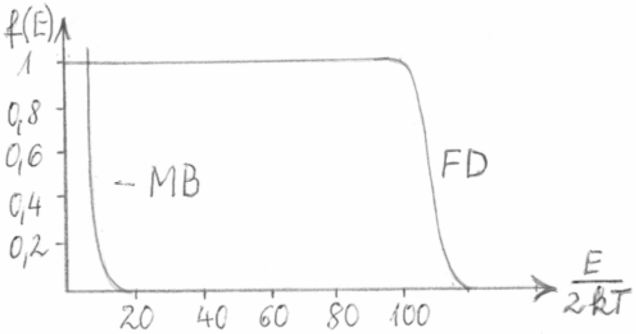
(For Maxw.-Boltzm. T=0 ∀ particles in ground state!)

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

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

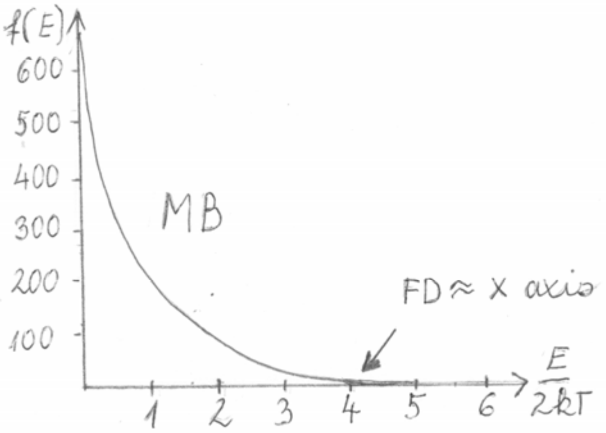
(electrons in metals $\Theta_F \approx 10^4$ °K)

Comparison of Maxwell-Boltzmann and Fermi-Dirac distribution at $T=10^{-2}\Theta_F$



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

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



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

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

$T=0$ $dn/dE=g(E)=$ 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 $U=\frac{3}{2}kNT$ $T=0 \rightsquigarrow U=0$ /

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

No. of electrons between E and E + dE

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

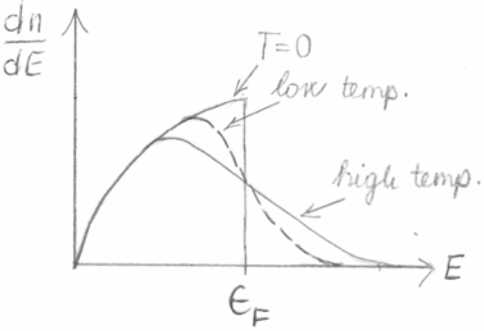
$$N=\int dn=\int_0^{\epsilon_F}\frac{dn}{dE}dE\rightsquigarrow$$

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

Depends on the electron density

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

ϵ_F for metals typically few eV



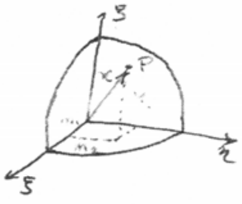
Number of states between 0 – E : N(E)

$\frac{1}{8}$ th of the volume of a sphere with radius $\varkappa = \sqrt{\frac{2mE}{\pi^2\hbar^2}} \cdot a$

$$N(E) = \frac{1}{8}\,\frac{4\pi\varkappa^3}{3} =$$

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

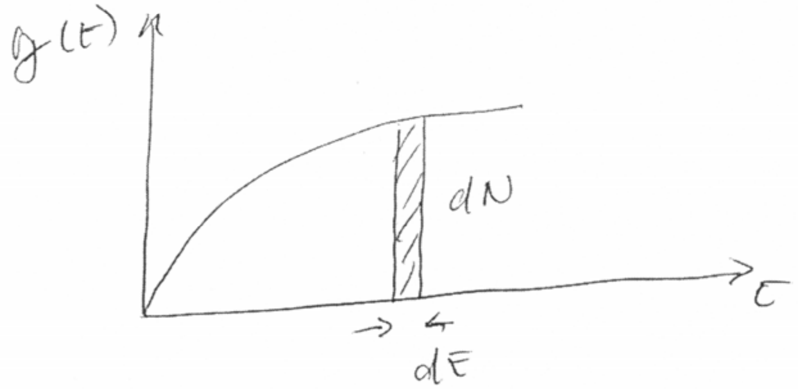
$$= \frac{8\pi V}{3h^3}\,(2m^3)^{1/2}\,E^{3/2}$$



$V = a^3$

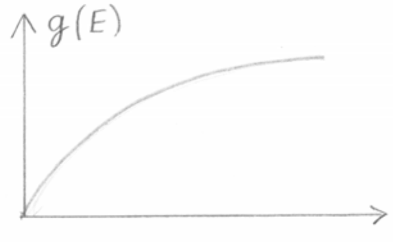
Density of states:

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

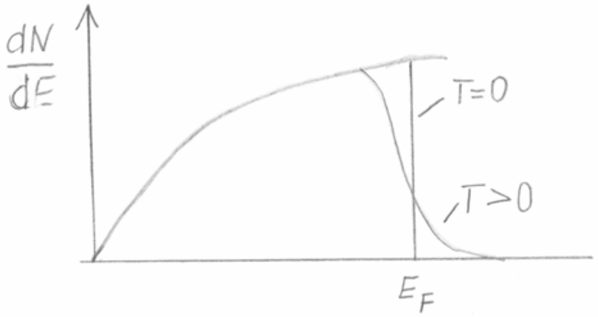


Free electrons - potential $k_0 x$

$$g(E) = \frac{4\pi v (2m^3)^{1/2}}{h^3} E^{1/2}$$



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



Electrons in periodic potential (crystal lattice)

$G(E)$ is different

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 $\left\{ \right.$ Energy: $h\nu$, momentum h/λ, indistinguishable, with each other non-interacting particles
Any number of particles with given energy $\Rightarrow$ **bosons** / angular momentum = 1 (circ. pol.)

The particle number in the cavity $\neq$ const. since the walls can absorb or emit ~

α arbitrary in thermal equilibr. Let $\alpha = 0$

In statistical equilibrium

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

Black body radiation
Planck's law

Possible energy states continuous

$$g_i \rightarrow g(E)dE$$

$$dn = \frac{g_i \, dE}{e^{E/kT} - 1}$$

. number of photons between E and $E + dE$

Density of states

$$g(E)dE = g(\nu)d\nu$$

since $E = h\nu$

2. Bose-Einstein statistics

Identical and indistinguishable particles, for the system of which the exclusion principle $\not\downarrow$ ~> there can be any number of particles in the same state

The wavefunction of the system is symmetric

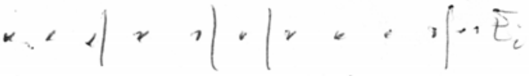
Particles with integer spin (0, 1, ..) e.g. ^{4}He nucleus, H_2 ..

system of even number of half spin particles, photon

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 ~> the number of distinguishable distributions is

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



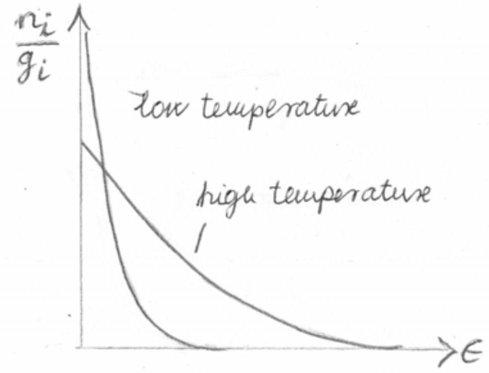
n_i particles
g_i states → $g_i - 1$ walls

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

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

– Its maximum corresponds to the statistical equilibrium

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



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

$$N = \sum_i n_i \rightsquigarrow \alpha$$

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

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

In a cavity with volume V the nubes 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 $\quad E(\nu) = \frac{h\nu}{V}\frac{dn}{d\nu}$

$$\varepsilon(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{kT}} - 1}$$ Planck's law for the blackbody radiation

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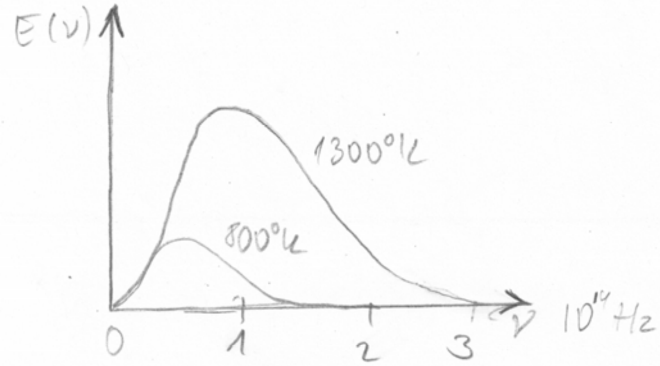
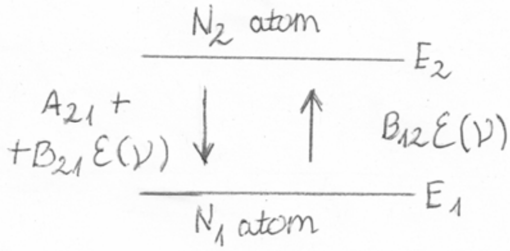
Considering the electromagnetic radiation as system of particles following Bose-Einstein statistics we get a spectrum corresponding to experimental results!



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

$B_{12}\ \varepsilon(\nu)$

$B_{12} = W(1\to 2)$ 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-Boltzm 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

$B_{12} = B_{21}$ $\qquad A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21}$ ← 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

$$\frac{\text{Prob emission/unit time}}{\text{Prob absorption/unit time}} = \frac{[A_{21} + B_{21}(\varepsilon(\nu))]N_2}{B_{12}\,\varepsilon(\nu)\,N_1} =$$

$$= \left(1 + \frac{A_{21}}{B_{21}(\varepsilon(\nu))}\right)\frac{N_2}{N_1}$$

If the system of atoms is <u>not</u> 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

Solids

Atoms or molecules tightly packed in fixed positions

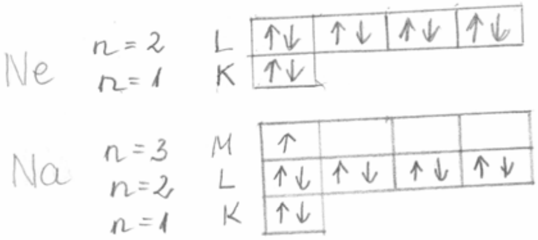
Forces: electromagnetic (on the order of molecular bonds)

Constant volume and shape in a wide range of p, T

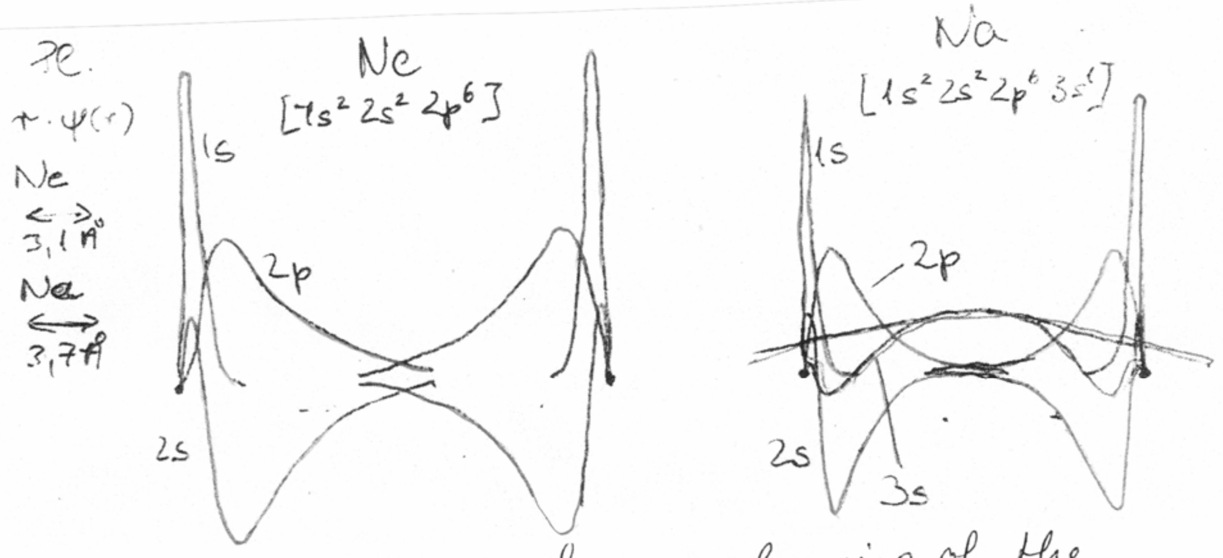
Atomic (molecular) properties strongly influenced by the interaction with neighbours.

Regular, periodic arrangement: crystal lattice

Description: according to the laws of quantum mechanics → stable nucleus – electron configuration (similar to molecules, No. of particles higher!



Types of solids



Metallic properties when overlapping of the atomic (molecular) electron wavefunctions is significant.

Covalent crystals : e.g. diamond localized e pairs
4 sp^3 hybrid wavefct. of C
(hard, not deformable)

Ionic crystals : e.g. NaCl
electrostatically attracted impenetrable balls

Hydrogen bond crystals : e.g. H_2O/ice
strongly polarised molecules
(dipole moments)

Molecular crystals : e.g. O_2, N_2
weak Van der Waals forces (induced fluctuations of dipole moment)

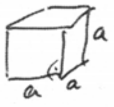
Crystal lattices : geometric periodic structure of atoms or group of atoms

Bravais lattice : describes the periodic arrangement

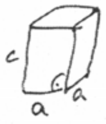
Body centered cubic (bcc)
Face centered cubic (fcc)

Lattice types:

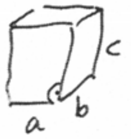
Symmetry operations
translation, rotation, mirroring & their combinations
Lattices can be classified into 14 different types:

Cubic


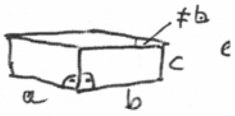
simple, face centered
body centered

Tetragonal


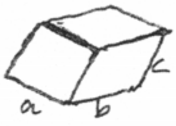
simple, centered

Orthorhombic


simple, base centered,
body cent., face centered

Monoclinic


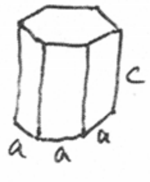
simple, centered

Triclinic


simple

Trigonal

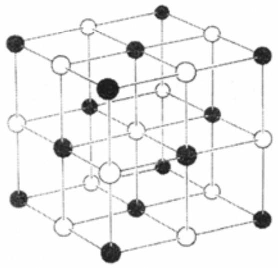

simple

Hexagonal


Crystal structure: lattice with base

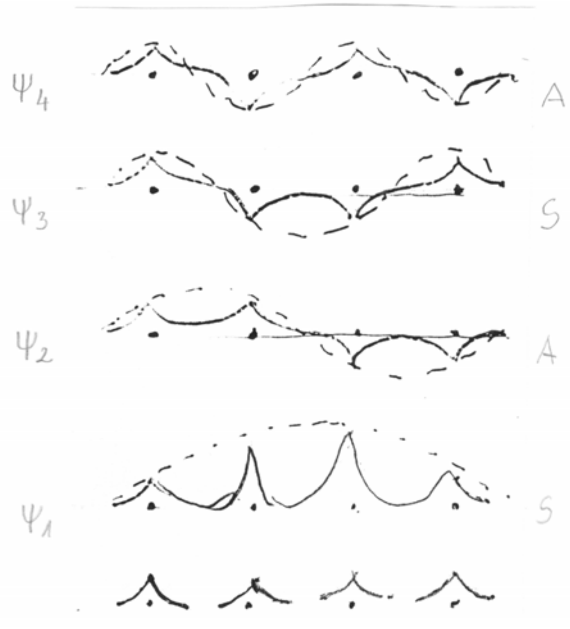
Base: group of atoms or molecules
located at a lattice point

E.g.: NaCl
face centered cubic
by ●—○ base

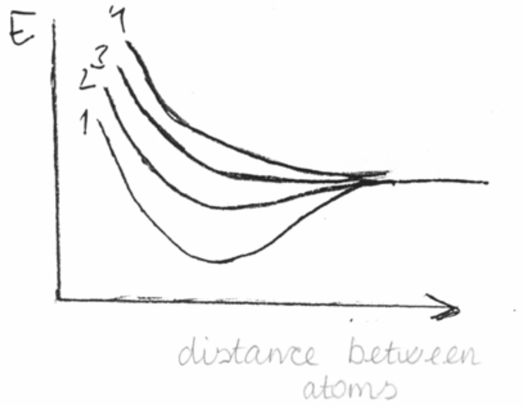


Conjugated molecules non-localized electrons

C_4H_6 Butadiene sp^2 hybrids
4pz electrons → π bond
orbitals by linear combina-
tion of atomic orbitals
LCAO



4 electrons from ∀ C atom
in the π bond ⇒ 8 states

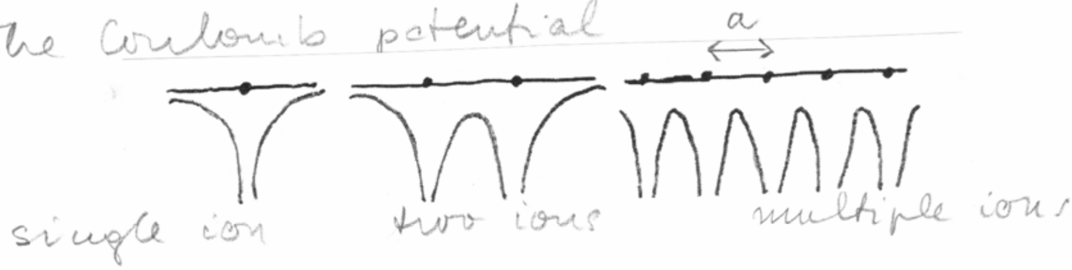


Energy levels

Band theory

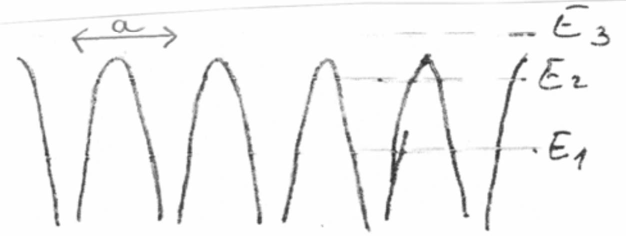
Behaviour of electrons in solids

The Coulomb potential



Solution: Schrödinger equation + exclusion principle

Preliminaries



E_1 electon energy: bond to the ion, localized

E_2 electon energy: electron tunnel through the potential barriers

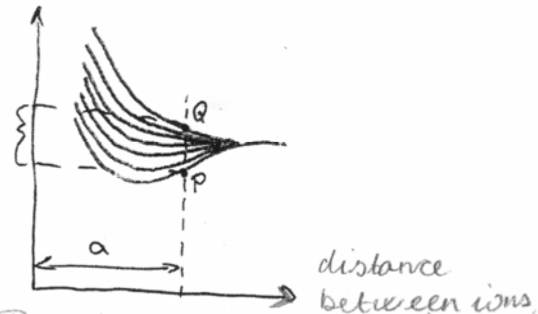
E_3 electon energy: "quasi-free electron"
These determine collective properties of solids (e.g. electric and heat conduction)
proved the bonds (in conductors)

Possible energy levels:

We have seen at molecules: the atomic levels split to N sublevels where N is the number of atoms

The same happens at solids:

N energy curves



Distance between ions = a

Possible energies between P and Q

N large → "continuous band"

Pauli principle: in a band formed by a given atomic state 2N electrons can occupy

s, p, d bands / corresponding to the atomic state

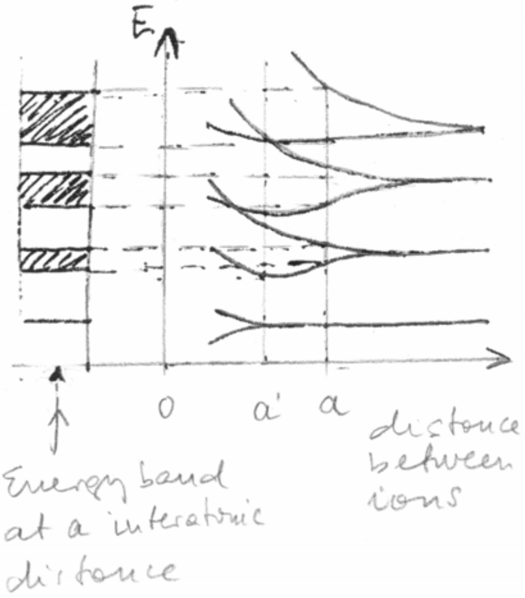
Multiple bands

From higher levels:

The bands start to form at higher interatomic distance because between the more extended wave-functions already overlap

At smaller a (e.g. a')

the bends can overlap



Bends from filled shells: localized electrons

They do not contribute to the properties of the solid

Important: external shell with the valence electrons

↓

The bend formed from these

↙ ↘

Not filled

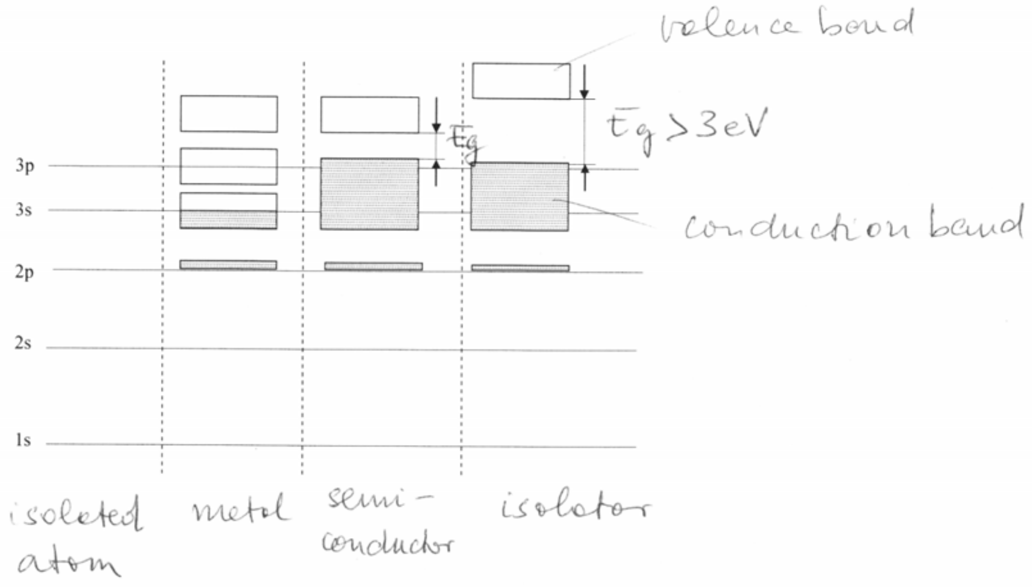
Conduction band

Filled

Valence band

The bend corresponding to the next higher level: conduction band

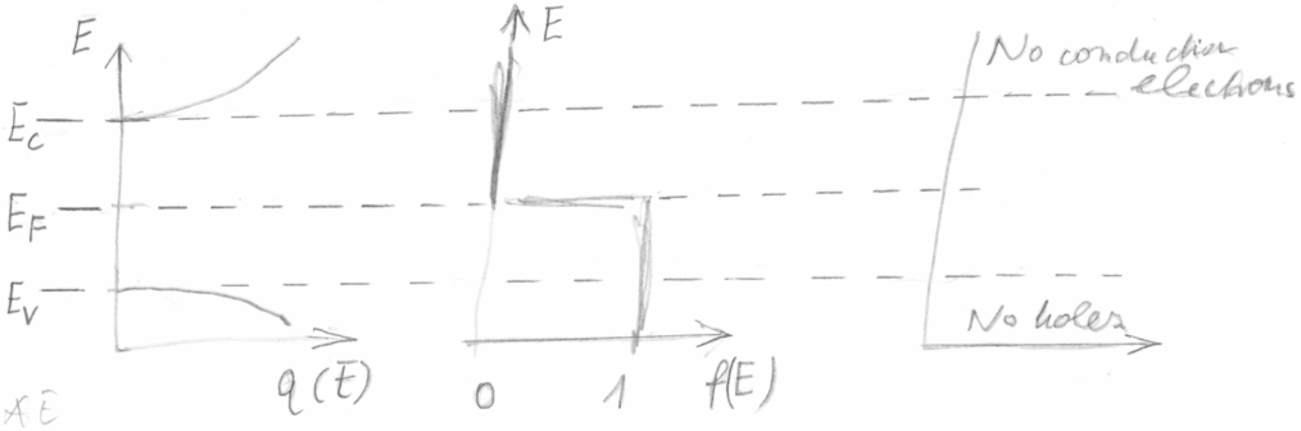
Broadening of energy levels



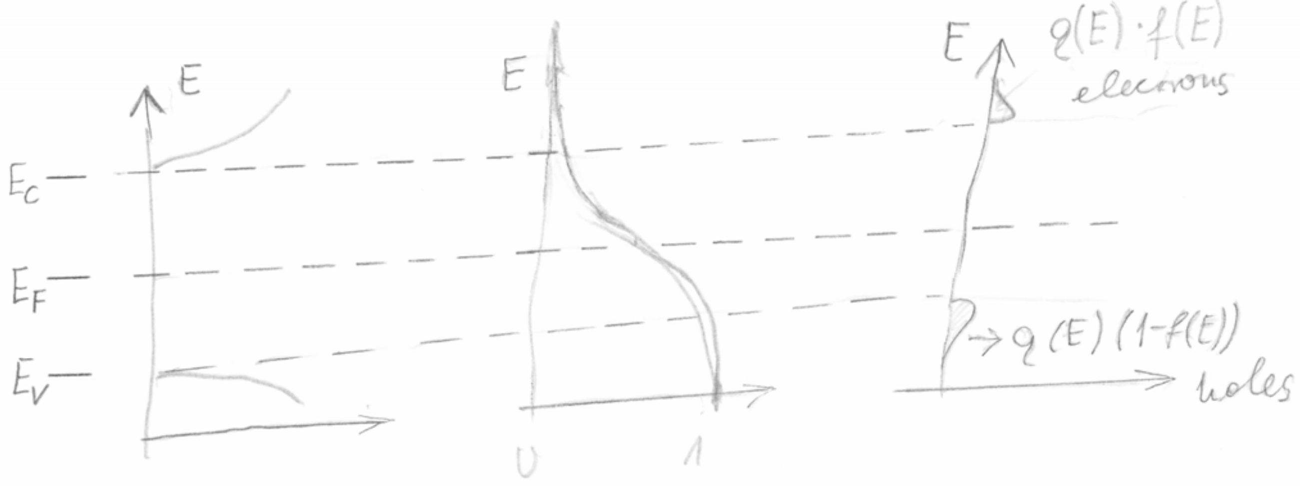
Conductivity $[\Omega \text{cm}]^{-1}$ 10^6 $10^3 - 10^{-6}$ 10^{-12}

Semiconductors : energy level structure can
be manipulated by
doping
structuring (super lattices
quantum dots etc.)

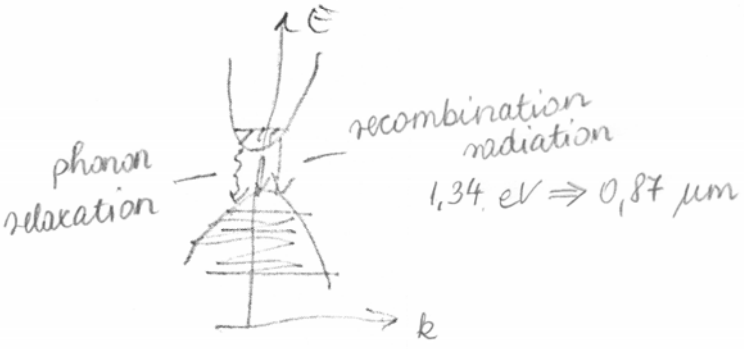
T=0


E
E_C
E_F
E_V
q(E)
E
0
1
f(E)
No conduction electrons
No holes

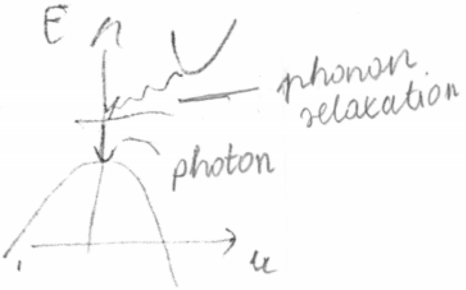
T>>0


E
E_C
E_F
E_V
E
0
1
E
q(E)·f(E)
electrons
→ q(E)(1−f(E))
holes

Excitation and decay



GaAs
direct bandgap



Si
indirect bandgap

Intrinsic semiconductors

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

E_F - Fermi energy ⇒ probability that the energy is there is $\frac{1}{2}$

density of states $\rho(E) = \left(\frac{1}{2\pi^2}\right)\left(\frac{2m_c}{\hbar^2}\right)^{3/2} E^{1/2} dt$

Total no. of electron $n_c = \int_0^\infty f(E)\rho(E)\,dE$

Total no. of holes $n_h = \int_0^\infty (1-f(E))\rho(E)\,dE$

Extrinsic semiconductors

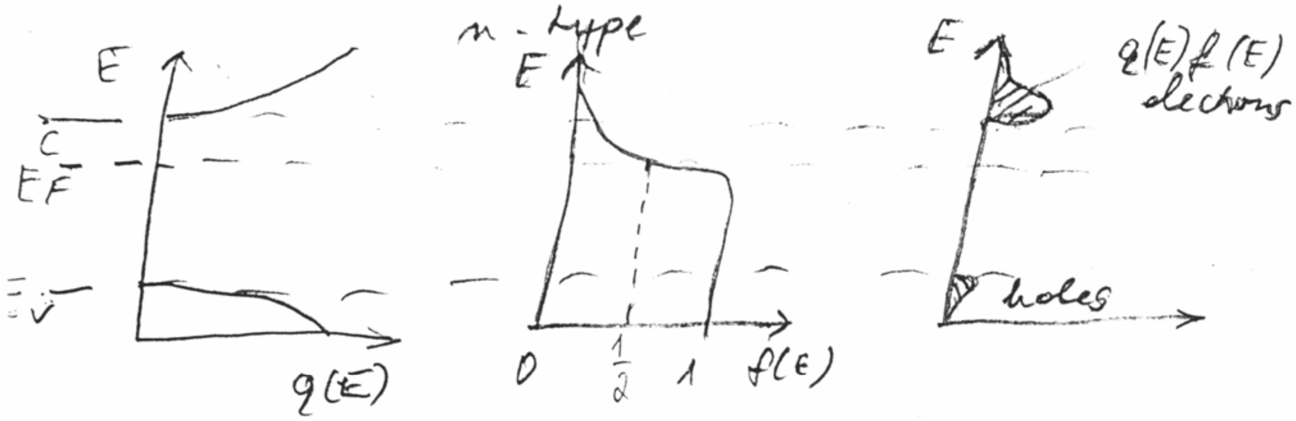
doping n type : energy levels near the conduction band
p type : energy levels near the valence band

GaAs, P n doped S, Se, Te
p doped Be, Zn, Cd

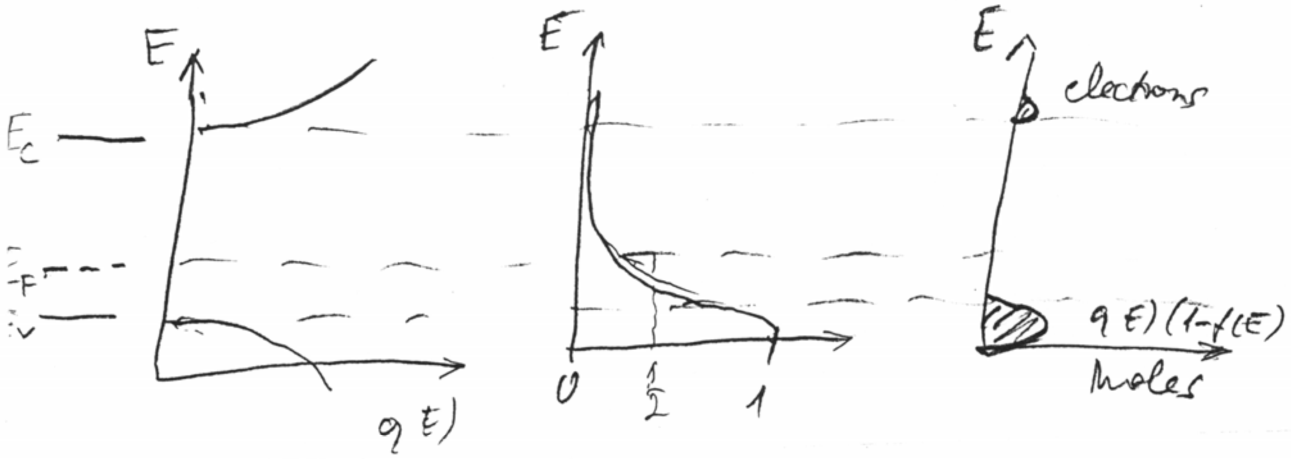
Doping : Fermi level shifts : n → toward cond. band
p → toward valence band

$T \gg 0$

n - type



p type

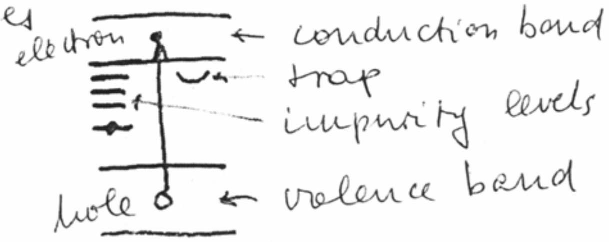


Luminescence

Electron excitation (by absorption of radiation, electron bomb. etc)
Return to ground state : multiple processes possible
Radiative transition : the solid emits due to the radiative excitation → luminescence

Impurities and defects of lattice are important

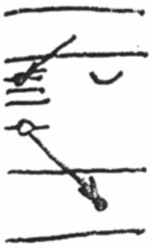
Processes



valence → conduct. el. exc.
hole remains in vel. band
in a clean and regular lattice electron returns to vel. band

time delay: el. and hole have different mobilities and move to opposite directio

– Impurities : energy levels in the gap

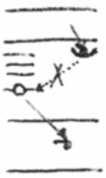


valence → conduct. electron excitation
electron from the low lying impurity level may recombine with the hole in the valence band
An electron from the conduction band may drop to the higher (empty) impurity level
Low energy transitions
Infrared

Continuing the former process the electron may drop from the high impurity level to the low impurity level → radiation : luminescence

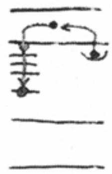
$E_{em} < E_{exc}$

Other possible processes



Following excitation the electron drops into a trap — transition to lower impurity levels is forbidd metastable state

Some other mechanism is needed



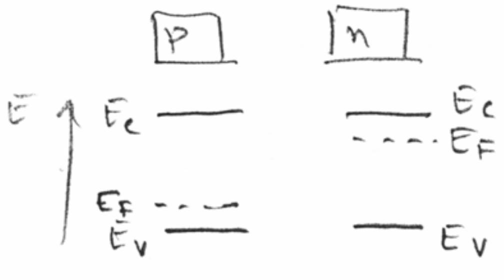
electron must get back to the conduction band — this is time consuming — from there luminescent transition.

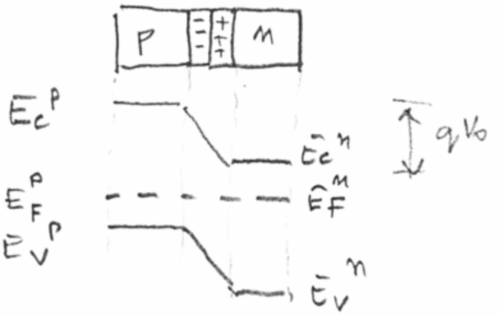
This is the <u>phosphorescence</u>

Phosphor materials e.g. ZnS
electron tubes
electron excitation
NaJ(Tl)
scintillation detector
(γ ray excitation)

p-n junction : recombination radiation

n and p type material in contact



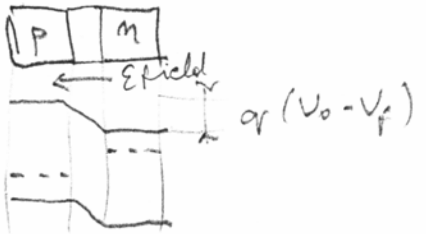


in contact: excess electrons from n → flow to p (fill the holes)

→ space charge – stops the flow (V_0) → barrier

Fermi levels equalize

applying electric field (+ to the p → forward bias) V_f



Barrier reduced

current flows

electrons and holes recombine

→ radiation

↓

LED, lasers

this structure: homojunction – too large current density

heterojunction

quantum well

gain/index guiding