

Structure of Matter

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1 Light and matter

1.1 Maxwell equations in differential form

in vacuum with charge- ρ and current density \vec{j}

$$\begin{aligned}\nabla \times \vec{E} &= -\frac{\partial}{\partial t} \vec{B} & \nabla \cdot \vec{E} &= \frac{1}{\epsilon_0} \rho \\ \nabla \times \vec{B} &= \frac{1}{c^2} \frac{\partial}{\partial t} \vec{E} + \mu_0 \vec{j} & \nabla \cdot \vec{B} &= 0\end{aligned}$$

with

\vec{E} : electric field, \vec{B} : magnetic induction

$\epsilon_0 = 8.8542 \cdot 10^{-12} \frac{\text{As}}{\text{Vm}}$ Vacuum permittivity,

$\mu_0 = 12.566 \cdot 10^{-7} \frac{\text{Vs}}{\text{Am}}$ Vacuum permeability,

$c = 2.99792458 \cdot 10^8 \frac{\text{m}}{\text{s}}$ speed of light in vacuum.

In above equation we have used the nabla operator ∇ , which can be represented in cartesian coordinates as $\nabla = \left(\vec{e}_x \frac{\partial}{\partial x}, \vec{e}_y \frac{\partial}{\partial y}, \vec{e}_z \frac{\partial}{\partial z} \right)$ with the unit vectors $\vec{e}_{x/y/z}$. The vector operations curl and divergence applied to a vector field \vec{a} can formally be expressed by a cross product

$$\nabla \times \vec{a} = \det \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ a_x & a_y & a_z \end{vmatrix} \text{ or a scalar product } \nabla \vec{a} = \frac{\partial a_x}{\partial x} + \frac{\partial a_y}{\partial y} + \frac{\partial a_z}{\partial z}, \text{ respectively.}$$

1.2 Wave equation

Mutual insertion of Maxwell's equations

$$\nabla \times \nabla \times \vec{E} = \nabla \times \left(-\frac{\partial}{\partial t} \vec{B} \right) = -\frac{\partial}{\partial t} \nabla \times \vec{B} = -\frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{E} - \mu_0 \frac{\partial}{\partial t} \vec{j}$$

results in the elimination of the magnetic induction.

A further transformation of the $\nabla \times \nabla \times$ operator

$$\nabla \times \nabla \times \vec{E} = \nabla \text{div} \vec{E} - \Delta \vec{E} = \nabla \frac{\rho}{\epsilon_0} - \Delta \vec{E}$$

results in the wave equation

$$\Delta \vec{E} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{E} = \underbrace{\nabla \frac{\rho}{\epsilon_0} + \mu_0 \frac{\partial}{\partial t} \vec{j}}_{\text{sources / drivers}},$$

where we have introduced the Laplacian operator $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. On the right hand side of the wave equation we find sources, which drive the field. Those sources of the electromagnetic field

- $\nabla \frac{\rho}{\epsilon_0}$ generates the quasi-static field around charges

- $\mu_0 \frac{\partial}{\partial t} \vec{t} = \mu_0 \frac{\partial}{\partial t} (\rho \vec{r}) \approx \mu_0 \rho \ddot{\vec{r}}$ complies with an accelerated charge

Accelerated ($\ddot{\vec{r}}$) charges radiate electromagnetic fields

1.3 Plane waves

Goal: to look for special solutions of the Maxwell-equations in areas without sources

$$(\rho = 0 \text{ and } \vec{j} = 0)$$

Ansatz: $\vec{E}(\vec{r}, t) = \text{Re} \left\{ \vec{E}_0 \exp \exp \left[i \left(\vec{k} \vec{r} - \omega t \right) \right] \right\}$ with $\vec{E}_0 \in C_3$ (complex field amplitude) and $\vec{k} \in C_3$ (wave vector)

By insertion into the wave equation one finds

$$\left(-\vec{k}^2 + \frac{\omega^2}{c^2} \right) \vec{E}_0 \exp \exp \left[i \left(\vec{k} \vec{r} - \omega t \right) \right] = 0.$$

Nontrivial solution require

$$\boxed{\vec{k}^2 = \frac{\omega^2}{c^2}} \text{ (dispersion relation of the vacuum)}$$

$\text{div } \vec{E} = 0$ is another requirement for the ansatz. It is fulfilled for $\vec{k} \vec{E}_0 = 0$.

To derive the strength of the magnetic induction we apply $\nabla \times \vec{E} = -\frac{\partial}{\partial t} \vec{B}$ to our ansatz

$$\nabla \times \text{Re} \left\{ \vec{E}_0 \exp \exp \left[i \left(\vec{k} \vec{r} - \omega t \right) \right] \right\} = \text{Re} \left\{ i \vec{k} \times \vec{E}_0 \exp \exp \left[i \left(\vec{k} \vec{r} - \omega t \right) \right] \right\} = -\frac{\partial}{\partial t} \vec{B}$$

resulting in:

$$\boxed{\vec{B} = \text{Re} \left\{ \vec{B}_0 \exp \exp \left[i \left(\vec{k} \vec{r} - \omega t \right) \right] \right\}} \text{ with } \boxed{\vec{B}_0 = \frac{1}{\omega} \vec{k} \times \vec{E}_0}$$

Electromagnetic waves in the vacuum are transversal with respect to the electric field and in the magnetic induction. Propagation vector, electric field and magnetic induction form an orthogonal trihedron.

1.4 Monochromatic fields

In optics monochromatic (single-coloured) fields are called stationary despite having a fast time dependence on only being constant in the average of time.

static lightfield: $\boxed{\vec{E}_{\text{real}}(\vec{r}, t) = \text{Re} \left[\vec{E}(\vec{r}) \exp(-i\omega t) \right]}$

From now on, we will only calculate with complex fields. The observable real fields can be generated by forming the real part.

a) Effect of time derivatives on monochromatic fields

$$\frac{\partial}{\partial t} \text{Re} \left[\vec{E}(\vec{r}) \exp(-i\omega t) \right] = \text{Re} \left[-i\omega \vec{E}(\vec{r}) \exp(-i\omega t) \right]$$

for monochromatic fields, time derivations are replaced by $-i\omega$.

Maxwell-equation for monochromatic fields

$$\begin{aligned} \nabla \times \vec{E} &= i\omega \vec{B} & \nabla \cdot \vec{E} &= \frac{1}{\epsilon_0} \rho \\ \nabla \times \vec{B} &= -\frac{i\omega}{c^2} \vec{E} + \mu_0 \vec{j} & \nabla \cdot \vec{B} &= 0 \end{aligned}$$

\vec{E} , \vec{B} , \vec{j} and ρ stand now for complex amplitudes.

b) Wave equation for monochromatic fields based on

$$\Delta \vec{E}_{\text{real}} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{E}_{\text{real}} = \nabla \frac{\rho_{\text{real}}}{\epsilon_0} + \mu_0 \frac{\partial}{\partial t} \vec{j}_{\text{real}} = \vec{q}_{\text{real}} \text{ with generic sources } \vec{q}_{\text{real}} \text{ one finds:}$$

$$\left(\Delta + \frac{\omega^2}{c^2} \right) \vec{E} = \vec{q}.$$

In free space ($\vec{j} = 0$, $\rho = 0$) this **Helmholtz-equation** is applied to all three components of the electric field ($u = E_{x/y/z}$) as

$$\left(\Delta + \frac{\omega^2}{c^2} \right) u(\vec{r}) = 0$$

A special solution for a point-like source or δ -excitation

$$\left(\Delta + \frac{\omega^2}{c^2} \right) u(\vec{r}) = \delta(\vec{r}) \text{ is a spherical wave (Huygens principle) } u(\vec{r}) = -\frac{1}{4\pi} \frac{e^{ikr}}{r} \text{ with } r = \sqrt{x^2 + y^2 + z^2} = |\vec{r}| \text{ and } k = \omega/c$$

c) Energy flux / Poynting-vector

The energy flux caused by electromagnetic fields is described by the Poynting-vector \vec{s} . In

general $\vec{s} = \frac{1}{\mu_0} \vec{E}_{\text{real}} \times \vec{B}_{\text{real}}$ contains both the electric field \vec{E}_{real} and the magnetic induction \vec{B}_{real} . In monochromatic lightfields both oscillates with the same frequency. Hence, also the magnetic induction can be expressed like $\vec{B}_{\text{real}}(\vec{r}, t) = \text{Re} \left[\vec{B}(\vec{r}) \exp(-i\omega t) \right]$.

The energy flux of monochromatic fields now contains stationary and fast oscillating terms as

$$\begin{aligned} \vec{s} &= \frac{1}{\mu_0} \frac{1}{2} \left(\vec{E} e^{-i\omega t} + \vec{E}^* e^{i\omega t} \right) \times \frac{1}{2} \left(\vec{B} e^{i\omega t} + \vec{B}^* e^{-i\omega t} \right) \\ &= \frac{1}{\mu_0} \frac{1}{4} \underbrace{\left(\vec{E} \times \vec{B}^* + \vec{E}^* \times \vec{B} \right)}_{\text{static}} + \frac{1}{4} \underbrace{\left(\vec{E} \times \vec{B} e^{-2i\omega t} + \vec{E}^* \times \vec{B}^* e^{2i\omega t} \right)}_{\text{fast oscillating}}. \end{aligned}$$

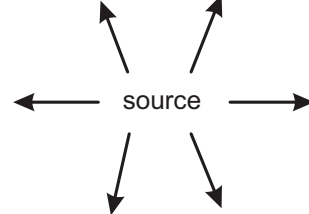
Optical instruments cannot resolve the fast oscillation in the energy flux of optical fields ($\approx 10^{15}$ Hz) and therefore record a time averaged Poynting-vector $\langle \vec{s} \rangle$, that only contains

the static part.

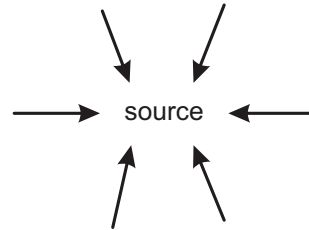
$$\langle \vec{s} \rangle = \frac{1}{2\mu_0} \text{Re} \left(\vec{E} \times \vec{B}^* \right)$$

We now study the energy flux balance by calculating the divergence of $\langle \vec{s} \rangle$, while keeping in mind that it stands for a local generation or absorption of electromagnetic energy as

$\text{div} \langle \vec{s} \rangle > 0 \Rightarrow$ generation of electromagnetic energy



$\text{div} \langle \vec{s} \rangle < 0 \Rightarrow$ absorption of electromagnetic energy



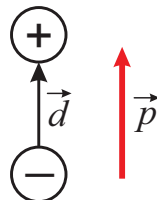
energy flux balance

$$\begin{aligned} \text{div} \langle \vec{s} \rangle &= \frac{1}{4\mu_0} \nabla \left[\vec{E} \times \vec{B}^* + cc \right] & cc : \text{ complex conjugate} \\ &= \frac{1}{4\mu_0} \vec{B}^* \nabla \times \vec{E} - \frac{1}{4\mu_0} \vec{E} \nabla \times \vec{B}^* + cc \\ &= \frac{1}{4\mu_0} \vec{B}^* i\omega \vec{B} - \frac{1}{4\mu_0} \vec{E} \left[+i\omega \frac{1}{c^2} \vec{E}^* + \mu_0 \vec{j}^* \right] + cc \\ \text{note: } \frac{i\omega}{4\mu_0} \vec{B} \vec{B}^* + cc &= \frac{i\omega}{4\mu_0} |\vec{B}|^2 - \frac{i\omega}{4\mu_0} |\vec{B}|^2 = 0 \\ &= -\frac{1}{4} \left[\vec{E} \vec{j}^* + \vec{E}^* \vec{j} \right] \end{aligned}$$

1.5 Single scatterer

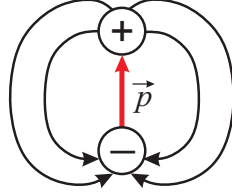
1.5.1 The oscillating dipole

Two point charges of opposite sign (charges $\pm q$ in distance \vec{d} form a dipole $\vec{p} = q\vec{d}$.



In general one finds the dipole moment \vec{p} as first element of a multipole expansion of a charge distribution (0. moment: charge, 1. moment: dipole, 2. moment: quadrupole ..., see lecture

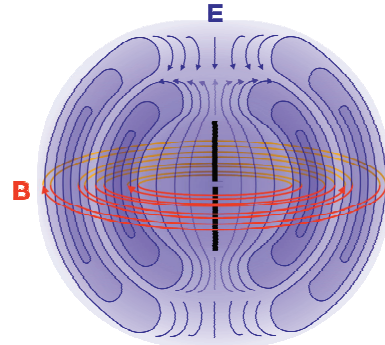
on electrodynamics or John D. Jackson "Classical Electrodynamics" chap. 4). The dipole is surrounded by an electric field



Natural dipoles are often extremely small. Hence, it makes sense to study the limiting case of a so-called point dipole, where the dipole moment \vec{p} is kept constant, but the extension of the dipole is assumed to vanish ($\vec{d} \rightarrow 0$).

In optics we deal with oscillating fields and therefore induced dipoles also oscillate like $\vec{p}_{\text{real}} = \vec{p}_0 \cos(\omega t) = \text{Re}(\vec{p}_0 e^{-i\omega t})$. The permanent inversion of the dipole moment requires the electric field around the dipole also to change sign periodically. Because this sign change can only travel with the speed of light waves of different polarity emerge from the dipole. The consequence is radiation.

The farfield of a Hertzian (infinitesimal $\vec{d} \rightarrow 0$ oscillating) dipole at $\vec{r} = 0$ is given by $\vec{E}(\vec{r}) = -\frac{\omega^2}{c^2} \frac{1}{4\pi\epsilon_0} \vec{n} \times (\vec{n} \times \vec{p}_0) \frac{e^{ikr}}{r}$ with $r = |\vec{r}|$, $\vec{n} = \frac{\vec{r}}{r}$ and $k = \frac{\omega}{c} = \frac{2\pi}{\lambda}$.



Discussion of the terms

- $\frac{e^{ikr}}{r}$
 - spherical wave (huygens principle)
 - the farfield declines like $1/r$ and the emitted energy density by $1/r^2$
- $\vec{n} \times (\vec{n} \times \vec{p}_0)$
 - there is no radiation along the dipole axis (for \vec{n} respectively \vec{r} parallel to \vec{p}_0 $\vec{n} \times \vec{p}_0$ disappears). The field intensity is proportional to the sine of the angle between \vec{n} and \vec{p}_0 .
 - the emitted field is polarized in the plane of \vec{n} and \vec{p}_0 and perpendicular to \vec{n} because $\vec{n} \times (\vec{n} \times \vec{p}_0) = \vec{n}(\vec{n} \cdot \vec{p}_0) - \vec{p}_0(\vec{n} \cdot \vec{n}) = \vec{n}(\vec{n} \cdot \vec{p}_0) - \vec{p}_0$

- ω^2

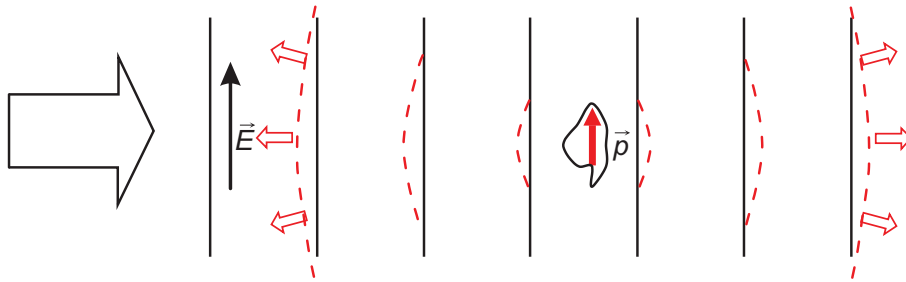
- the frequency dependence of the radiation is a consequence of the fact, that radiation is proportional to acceleration of the involved charges.
- the emitted power is $\sim \omega^4$.

1.5.2 The driven dipole

For the high frequencies in optics ($\approx 10^{15}$ Hz) dipoles can only be stimulated by the optical field. The incident optical field exerts a force on the present single charges $\vec{F} = q\vec{E}$ and induces dipoles. The induced dipoles oscillate with the frequency of the incident field and radiate perpendicular to the dipole axis.

1.5.3 Scattering

- a) polarized light For small or spherical clusters the axis of the induced dipole points in the



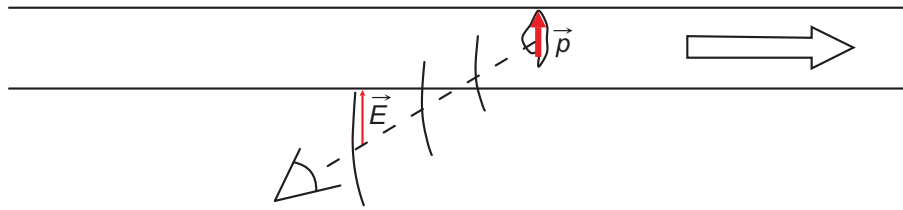
direction of the polarization of the incident light. No scattering occurs in the direction of the dipole axis and therefore not in the direction of the polarization of the incident field as well.

- b) nonpolarized light

Nonpolarized light is a superposition of fields with different polarization, that are all polarized perpendicular to the direction of propagation. An observer alongside the beam will only see the scattered light, that is polarized perpendicular to the plane formed by the beamaxis and the observer. Hence, although the initial light was unpolarized the scattered field usually shows a preferred direction of polarization.

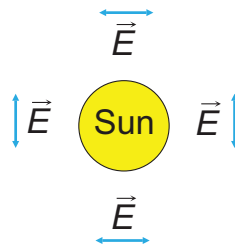
- c) frequency sensitivity of scattering

Blue light is scattered far stronger than red light, because the scattered power is $\sim \omega^4$.



d) the sky as a scattering phenomenon

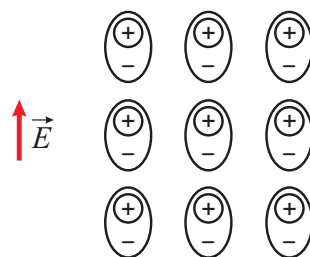
The light we receive from the sky is sun light, which is scattered by stochastic density fluctuations in the air. Due to the enhanced scattering of blue high frequency radiation we experience the sky as blue. The light from the sky is polarized azimuthal around the sun.



1.6 Field propagation in homogeneous matter

1.6.1 Polarization and current

We will speak of homogeneous matter, if inhomogenities are smaller than $\approx \lambda/10$. The excitation by a plane wave induces homogeneously distributed and with the frequency of the light oscillating dipoles. Scattering cannot appear because no "scattering direction" is singled out in

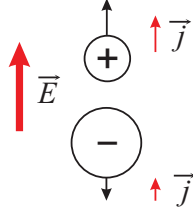


a homogeneous material. The material does not know in which direction it should scatter. The original and the scattered field form a collective wave with new properties.

Action of the induced dipoles

- Local charge clouds with dimensions $\ll \lambda/10$ do not influence the mean field propagation. Because the whole charge is zero no long ranging fields are induced by the displaced charges

- Induced currents (shifting charges in the dipole) **cannot** be neglected.



Analysis of the induced currents:

Each dipole participates to a small elementary current: $\frac{d}{dt}\vec{p}_{\text{real}}(t) = q\frac{d}{dt}\vec{d} = \vec{j}_{\text{microscopic}}$ Changing the macroscopic polarization $\vec{P}_{\text{real}} = N\vec{p}_{\text{real}}$ (N : dipole density) results in a macroscopic current, that oscillates with the frequency of the light. $\frac{d}{dt}\vec{P}(t)_{\text{real}} = \vec{j}_{\text{polarization}_{\text{real}}}$

1.6.2 Modified Maxwell's equations

The current density due to the oscillating polarization is inserted into Maxwell's equations $\nabla \times \vec{B}_{\text{real}} = \frac{1}{c^2} \frac{\partial}{\partial t} \vec{E}_{\text{real}} + \mu_0 \vec{j}_{\text{polarization}} = \mu_0 \frac{\partial}{\partial t} (\varepsilon_0 \vec{E}_{\text{real}} + \vec{P}_{\text{real}})$ by using $\varepsilon_0 \mu_0 = \frac{1}{c^2}$. For monochromatic fields ($\partial/\partial t$ becomes $-i\omega$):

$$\nabla \times \vec{B} = -i\omega\mu_0 (\varepsilon_0 \vec{E} + \vec{P})$$

applies, whereas the dielectric displacement $\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$ occurs. For monochromatic fields of moderate intensity and in isotropic (not depending on orientation) media $\vec{P}(\omega) = \varepsilon_0 \chi(\omega) \vec{E}(\omega)$ applies. Therefore the dielectric displacement is $\vec{D}(\omega) = \varepsilon_0 \varepsilon(\omega) \vec{E}(\omega)$.

1.6.3 Modified wave equations

$$\nabla \times \nabla \times \vec{E} = \text{rot}(i\omega \vec{B}) = i\omega \left[-i\frac{\omega}{c^2} \varepsilon \vec{E} \right] = \varepsilon \frac{\omega^2}{c^2} \vec{E} = \frac{\omega^2}{c'^2} \vec{E} \text{ with } c' = \frac{c}{\sqrt{\varepsilon}} \text{ for } \varepsilon > 0 \text{ and } \varepsilon \text{ real.}$$

Because of the induced dipole currents in the material, the speed of light c is changed to c' and so the wavelength is modified from $\lambda = 2\pi c/\omega$ to $\lambda' = 2\pi c'/\omega = \lambda/\sqrt{\varepsilon}$.

The transformation of the $\nabla \times \nabla \times$ term is inserted like $\nabla \times \nabla \times \vec{E} = (\nabla \text{div} - \Delta) \vec{E}$.

In a homogeneous material without external charges the $\text{div } \vec{E} = \frac{1}{\varepsilon_0} \rho$ term is only sensitive to the microscopic charge clouds around the individual dipoles. In the macroscopic mean and in the absence of external charges $\text{div } \vec{E} = 0$ can be set for homogeneous materials and one finds:

$$\left(\Delta + \varepsilon \frac{\omega^2}{c^2} \right) \vec{E}(\vec{r}) = 0$$

2 Optical properties of solids

2.1 The Drude-Model

Idea: Description of the material as an ensemble of oscillators driven by the optical field.

bound charges = lines oscillators

optical field = driving force

polarization = induced displacement

Evolution equation of the elongation \vec{d} of an "oscillator"

$$\underbrace{m \frac{d^2}{dt^2} \vec{d}}_{\text{inertia}} + \underbrace{m \gamma \frac{d}{dt} \vec{d}}_{\text{attenuation}} + \underbrace{m \omega_0^2 \vec{d}}_{\text{restoring force}} = \underbrace{q \vec{E}_{\text{real}}}_{\text{driver}}$$

with an eigenfrequency ω_0 , the attenuation ratio γ , the mass m and the charge q . The macroscopic dipole moment induced by motion is $\vec{p} = q \vec{d}$. The macroscopic polarization results from multiplication with the dipole density N as $\vec{P}_{\text{real}} = N \vec{p}$ (Caution \vec{p} and \vec{P}_{real} have different units!)

Therefore, the equation of motion of the macroscopic polarization is

$$\left[\frac{d^2}{dt^2} + \gamma \frac{d}{dt} + \omega_0^2 \right] \vec{P}_{\text{real}} = N \frac{q^2}{m} \vec{E}_{\text{real}}$$

For a monochromatic driver field, the complex amplitude of the polarization is

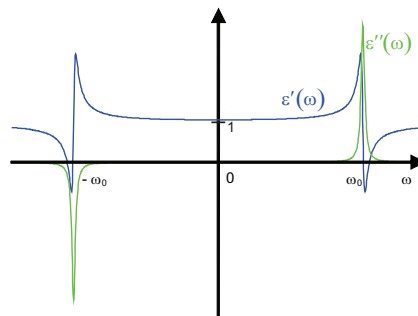
$$\vec{P}(\omega) = \varepsilon_0 \frac{f}{\omega_0^2 - \omega^2 - i\gamma\omega} \vec{E}(\omega)$$

with the strength of the oscillator $f = \frac{1}{\varepsilon_0} \frac{q^2 N}{m}$.

Because $\vec{P}(\omega) = \varepsilon_0 \chi(\omega) \vec{E}(\omega)$ applies, the complex susceptibility function is found as

$$\chi(\omega) = \frac{f}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

From the susceptibility follows the relative permittivity as $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = 1 + \frac{f}{\omega_0^2 - \omega^2 - i\gamma\omega}$



In general, it applies that

- The permittivity is heavily frequency sensitive, especially near resonances (dispersive)
- The real part / imaginary part of the permittivity is symmetric / antisymmetric in respect to $\omega = 0$.
- The imaginary part of the permittivity is only near resonances considerably different from zero (strong decline when shifting away from the resonance), while the real part is influenced by the resonance on a far greater frequency range.

2.2 The effect of a complex permittivity

1. Susceptibility and conductivity

$$\vec{j}_{\text{real}} = \frac{d}{dt} \vec{P}_{\text{real}} \quad \Rightarrow \quad \vec{j} = -i\omega \vec{P}$$

$$\begin{array}{ccc} \vec{j} = \sigma \vec{E} & & \vec{P} = \epsilon_0 \chi(\omega) \vec{E} \\ \uparrow & & \uparrow \\ \text{conductivity} & & \text{susceptibility} \end{array}$$

$$\sigma \vec{E} = -i\omega \epsilon_0 \chi(\omega) \vec{E} \quad \Rightarrow \quad \sigma = -i\omega \epsilon_0 \chi(\omega)$$

2. energy balance

$$\text{div } \langle \vec{s} \rangle = -\frac{1}{4} \left[\vec{E} \vec{j}^* + \vec{E}^* \vec{j} \right]$$

\uparrow

Time averaged pointing vector

$$\begin{aligned} \text{div } \langle \vec{s} \rangle &= -\frac{1}{4} [\sigma + \sigma^*] |\vec{E}|^2 \\ &= -\frac{1}{2} \text{Re}[\sigma] |\vec{E}|^2 & \text{Re}\sigma > 0 \Rightarrow \text{losses} \\ &= -\frac{1}{4} [-i\omega \epsilon_0 \chi + i\omega \epsilon_0 \chi^*] |\vec{E}|^2 \\ &= -\frac{\epsilon_0 \omega}{2} \text{Im}\chi |\vec{E}|^2 & \text{Im}\chi > 0 \Rightarrow \text{losses} \end{aligned}$$

In general, the Helmholtz-equation $(\Delta + \epsilon \frac{\omega^2}{c^2}) \vec{E}(\vec{r}) = 0$ describes the propagation of monochromatic fields in homogeneous and isotropic material. Solutions are, e.g., plane waves $\vec{E}(\vec{r}) = \vec{E}_0 \exp(i\vec{k}\vec{r})$, whose wave vector fulfills the dispersion relation $\vec{k}^2 = \epsilon \frac{\omega^2}{c^2}$. Depending on the frequency range three interesting cases develop:

1. ε is real (far from resonance)

\vec{k} can be. It is a "normal" wave.

2. ε is complex (near resonance)

$\vec{k} = \vec{k}_R + i\vec{k}_i$ is complex. It is a wave declining evanescent $\sim \exp(-\vec{k}_i \vec{r})$ in direction of \vec{k}_i . The not disappearing imaginary part of the permittivity causes a degradation of energy (absorption).

3. ε is complex (near resonance)

$$\vec{k}^2 = k_x^2 + k_y^2 + k_z^2 = -|\varepsilon| \frac{\omega^2}{c^2}$$

At least one of the three components of the wave vector is imaginary. An attenuation in the corresponding direction occurs. Nothing changes at it, even if ε has for a negative real part on imaginary part as well.

2.3 The susceptibility of real materials

Form of the resonance

The width of the resonance (width of the absorptionline) is determined by the attenuation and equals γ . Therefore materials with weak attenuation have a small absorptionline.

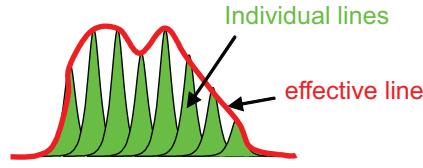
gases:

- weak interaction of the atoms/molecules
- weak attenuation ($\gamma = 1/T_{\text{attenuation}}$ with attenuation times between 100 ps and some nanoseconds)
- small absorptionlines (linewidth $< 10^{-3}$ nm)

solids:

- strong interaction of the individual oscillators
- homogeneous broadening through amplified attenuation ($\gamma = 1/T_{\text{attenuation}}$ with attenuation times around 10 fs and linewidth > 1 nm)
- inhomogeneous broadening by overlapping of many parallel lying niveaus

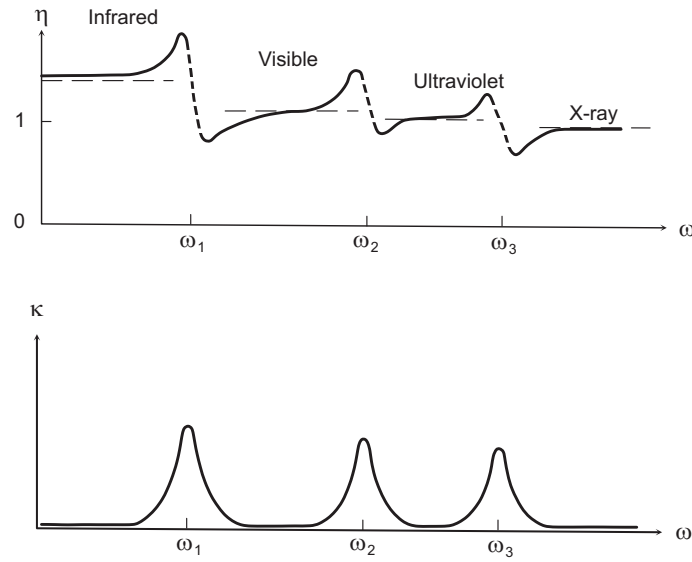
Influence of multiple resonances



Real systems always have multiple resonances for different resonance frequencies ω_m , which is why the Drude-model must be modified:

$$\varepsilon(\omega) = 1 + \sum_m \frac{f_m}{\omega_m^2 - \omega^2 - i\gamma_m\omega}$$

Typical distribution of $\text{Re}(\varepsilon)$ and $\text{Im}(\varepsilon)$ in a transparent matter (resonance width exaggerated).



Transparent matter in the visible spectral range

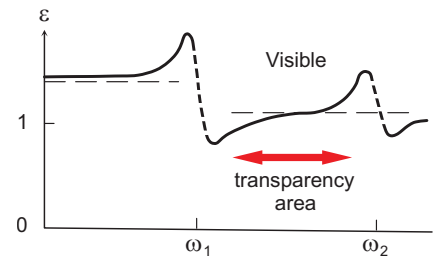
In transparency areas, one can usually restrict oneself to the effect of two parallel resonances and neglect the attenuation ($\gamma = 0$):

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{f_1}{\omega_1^2 - \omega^2} + \frac{f_2}{\omega_2^2 - \omega^2} \text{ for } \omega_1 < \omega < \omega_2$$

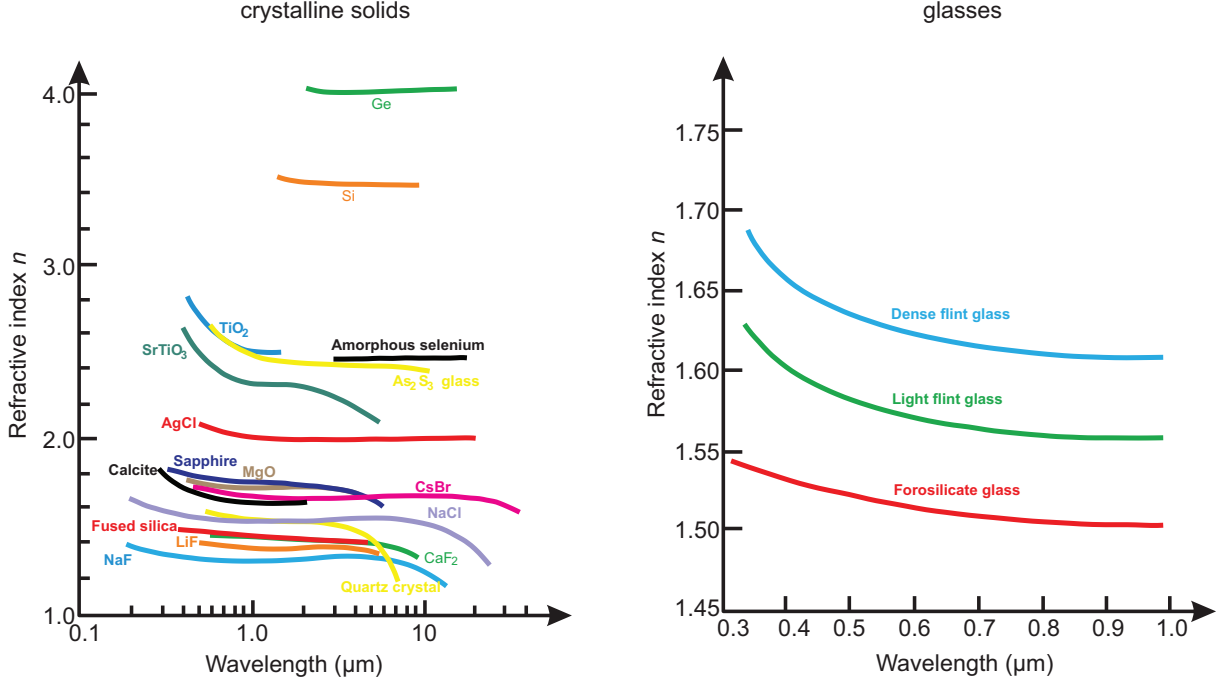
ε_∞ : influence of far away resonances

resonance 1: in infrared

resonance 2: in ultraviolet



In the majority of cases applies in the transparency area that $\frac{\partial \epsilon}{\partial \omega} > 0$, a behavior, that is called "normal" dispersion (dispersion = frequency sensitivity). Wavelength dependant refractive index



of various materials in their respective transparency areas.

2.4 Metals

Metals are characterized by a high density of free carriers. Therefore the restoring force is absent in the respective equation of motion:

$$\underbrace{m \frac{d^2}{dt^2}}_{\text{inertia}} \vec{d} + \underbrace{m\gamma \frac{d}{dt}}_{\text{attenuation}} \vec{d} = \underbrace{q\vec{E}_{\text{real}}}_{\text{driver}} \quad (\text{oscillator with an eigenfrequency } \omega_0 = 0)$$

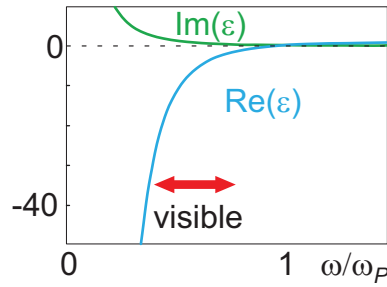
The formulas derived above can be directly assigned for metals. If we set $\omega_0 = 0$, the result is

$$\chi(\omega) = -\frac{q^2 N}{\epsilon_0 m} \frac{1}{\omega^2 + i\gamma\omega} = -\frac{\omega_P^2}{\omega^2 + i\gamma\omega} \quad \text{with a plasma frequency } \omega_P^2 = \frac{q^2 N}{\epsilon_0 m} \quad \text{and the relative permittivity}$$

$$\epsilon(\omega) = 1 - \frac{\omega_P^2}{\omega^2 + i\gamma\omega}$$

In general the permittivities of metals have

- a high absolute value (due to the high density of electrons),
- a negative real part for the visible spectral range,



- a noticeable imaginary part ($\text{Im}(\varepsilon) < |\text{Re}(\varepsilon)|$)
- a plasma frequency in the near ultraviolet spectral range

Example: Ag: for $\lambda = 1 \mu\text{m}$ $\text{Re}(\varepsilon) = -40$, $\text{Im}(\varepsilon) = 3$; plasma frequency: $\omega_P = 5.65 \times 10^{15} \text{ s}^{-1}$ according to a wavelength of $\lambda_P = 330 \text{ nm}$.

For $\omega < \omega_P$ and for negligible $\text{Im}(\varepsilon)$ ($\varepsilon(\omega) \approx 1 - \omega_P^2/\omega^2 < 0$) are least one wave vector component of plane wave $\vec{E}(\vec{r}) = \vec{E}_0 \exp(i\vec{k}\vec{r})$ with the dispersion relation $\vec{k}^2 = k_x^2 + k_y^2 + k_z^2 = -|\varepsilon|\frac{\omega^2}{c^2}$ is imaginary. An exponential attenuation in the corresponding direction occurs. Hence, below the plasma frequency the light cannot penetrate into the metal because electrons shield the optical field. Above the plasma frequency the electrons are not longer able to follow the fast oscillation of the optical field. The shield collapses and the metal behaves like a "normal" dielectric.

2.5 Optical Anisotropy

2.5.1 General considerations

up to now: isotropic materials

(optical properties independent of direction)

$$\left. \begin{aligned} \vec{P}(\omega) &= \varepsilon_0 \chi(\omega) \vec{E}(\omega) \\ \vec{D}(\omega) &= \varepsilon_0 \varepsilon(\omega) \vec{E}(\omega) \end{aligned} \right\} \begin{array}{l} \chi \\ \varepsilon \end{array} \text{ scalar}$$

$$\Rightarrow \vec{P} \parallel \vec{E} \text{ and } \vec{D} \parallel \vec{E}$$

now: anisotropic materials $\hat{=}$ direction dependent

optical properties

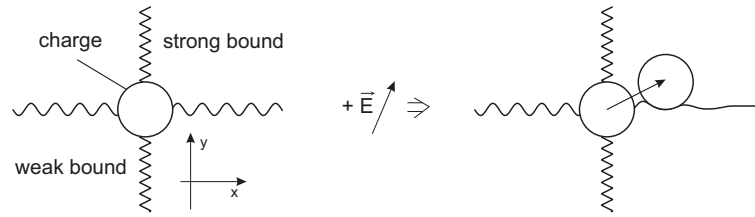
reason anisotropic lattice e.g. Quartz, LiNb_3 , CdS, Liquid crystals

\Rightarrow elongation different for electric fields pointing in x or y-direction

$\Rightarrow \vec{P}$ not necessarily parallel to \vec{E}

general notation

$$\vec{P} = \varepsilon_0 \hat{\chi} \vec{E} \text{ or } \vec{D} = \varepsilon_0 \hat{\varepsilon} \vec{E}$$



$\hat{\chi}, \hat{\varepsilon}$: 3×3 tensors

with components

$$D_i = \varepsilon_0 \sum_{j=1}^3 \varepsilon_{ij} E_j \quad (P_i \text{ analog})$$

lossless case: $\hat{\varepsilon}$ selfadjoint

$$\hat{\varepsilon} = \hat{\varepsilon}^+ \text{ or } \varepsilon_{ij} = \varepsilon_{ji}^*$$

\Rightarrow 3 orthogonal eigenvectors \vec{e}_i + real eigenvalues ε_i

$$\hat{\varepsilon} \vec{e}_i = \varepsilon_i \vec{e}_i \text{ with } \vec{e}_i \vec{e}_j = \delta_{ij} \text{ and } \varepsilon_i \text{ real}$$

physical meaning of the eigenvectors

- \vec{E} along the eigenvector ($\vec{E} = E_0 \vec{e}_i$)
 $\Rightarrow \vec{D} = \varepsilon_0 \varepsilon_i \vec{E} \Rightarrow \vec{D} \parallel \vec{E}$
- Directions of symmetry of the crystal

2.5.2 Optical classification of crystals

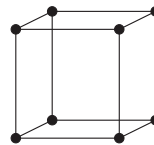
1. **Isotropic** \Rightarrow no preferred direction

- gases
- amorphous solids (e.g. glass)
- liquids

crystals: Three crystallographic equivalent orthogonal axes. Cubic crystals (*diamond, Si ...*)

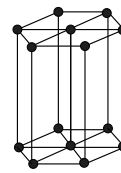
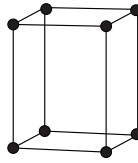
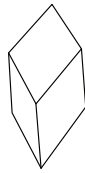
$$\varepsilon_1(\omega) = \varepsilon_2(\omega) = \varepsilon_3(\omega) = \varepsilon(\omega)$$

$$\rightarrow \vec{D} = \varepsilon_0 \varepsilon(\omega) \vec{E}$$



2. Uniaxial

Two linearly independent crystallographic equivalent directions. Trigonal (*quartz, lithiumniobate*), tetragonal, hexagonal. $\varepsilon_1(\omega) = \varepsilon_2(\omega) \neq \varepsilon_3(\omega)$

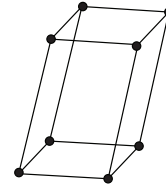
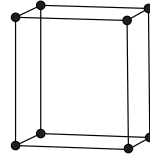


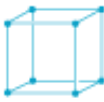




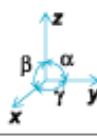









3. Biaxial

No crystallographic equivalent directions.

Orthorhombic, monoclinic, triclinic.

$$\epsilon_1(\omega) \neq \epsilon_2(\omega) \neq \epsilon_3(\omega) \neq \epsilon_1(\omega)$$



Bravais lattice cells	Axes and interaxial angles	Examples
   Cubic P Cubic I Cubic F	Three axes at right angles; all equal: $a = b = c; \alpha = \beta = \gamma = 90^\circ$	Copper (Cu), silver (Ag), sodium chloride (NaCl)
   Tetragonal P Tetragonal I	Three axes at right angles; two equal: $a = b \neq c; \alpha = \beta = \gamma = 90^\circ$	White tin (Sn), rutile (TiO₂), β-spodumene (LiAlSi₂O₆)
    P C I F Orthorhombic	Three axes at right angles; all unequal: $a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$	Gallium (Ga), perovskite (CaTiO₃)
  Monoclinic P Monoclinic C	Three axes, one pair not at right angles, of any lengths: $a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta$	Gypsum (CaSO₄ • 2H₂O)
 Triclinic P	Three axes not at right angles, of any lengths: $a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90^\circ$	Potassium chromate (K₂CrO₇)
 Trigonal R (rhombohedral)	Rhombohedral: three axes equally inclined, not at right angles; all equal: $a = b = c; \alpha = \beta = \gamma \neq 90^\circ$	Calcite (CaCO₃), arsenic (As), bismuth (Bi)
 Trigonal and hexagonal C (or P)	Hexagonal: three equal axes coplanar at 120°, fourth axis at right angles to these: $a_1 = a_2 = a_3 \neq c;$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Zinc (Zn), cadmium (Cd), quartz (SiO₂) [P]

3 Basic properties of dielectric functions

up to now: exclusive treatment of monochromatic fields $\vec{P}(\omega) = \varepsilon_0 \chi(\omega) \vec{E}(\omega)$. In case of arbitrary time progresses, the real fields are superpositions of many monochromatic fields

$$\vec{P}_{\text{real}}(t) = \int_{-\infty}^{+\infty} d\omega \vec{P}(\omega) e^{-i\omega t} = \int_{-\infty}^{+\infty} d\omega \varepsilon_0 \chi(\omega) \vec{E}(\omega) e^{-i\omega t},$$

whereas the single spectral amplitude is determined by

$$\vec{E}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \vec{E}_{\text{real}}(t) e^{i\omega t}$$

Substituting $\vec{E}(\omega)$ in the term of the polarization, it leads to

$$\begin{aligned} \vec{P}_{\text{real}}(t) &= \varepsilon_0 \int_{-\infty}^{+\infty} d\tau R(\tau) \vec{E}_{\text{real}}(t - \tau) \\ &= \varepsilon_0 \int_{-\infty}^{+\infty} d\omega \chi(\omega) \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt' \vec{E}_{\text{real}}(t') e^{-i\omega(t-t')} \\ &= \varepsilon \int_{-\infty}^{+\infty} dt' \vec{E}_{\text{real}}(t') \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \chi(\omega) e^{i\omega \underbrace{(t-t')}_\tau} \\ &= \varepsilon \int_{-\infty}^{+\infty} d\tau \vec{E}_{\text{real}}(t - \tau) R(\tau) \end{aligned}$$

with the response function $R(\tau) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \chi(\omega) e^{-i\omega \tau}$. The response function has to fulfill the following requirements:

1. R be real.
2. R must be causal, that means $R(\tau) = 0$ must apply for $\tau < 0$, otherwise the polarization $\vec{P}_{\text{real}}(t)$ at time t would be influenced by electric fields from the future $\vec{E}_{\text{real}}(t' > t)$.

Contrary the susceptibility can be generated from the response function by Fourier-transformation

$$\chi(\omega) = \int_{-\infty}^{+\infty} d\tau R(\tau) e^{i\omega \tau}$$

The requirements for R mentioned above affect χ too. In detail they result in the following relations

$$\begin{aligned}
1. \quad \chi(\omega) &= \chi(-\omega)^* = \left[\int_{-\infty}^{+\infty} d\tau R(\tau) e^{-i\omega\tau} \right]^* = \chi(-\omega)^* \\
2. \quad \chi(\omega) &= \frac{1}{i\pi} \lim_{\nu \rightarrow 0} \left[\int_{-\infty}^{\omega-\nu} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega}-\omega} + \int_{\omega+\nu}^{\infty} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega}-\omega} \right] = \frac{1}{i\pi} P \int_{-\infty}^{\infty} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega}-\omega}
\end{aligned}$$

where $P \int$: Cauchy principle value

The first relation applies generally if real variables are Fourier-transformed. It shows, that the space of negative frequencies ($\omega < 0$) contains no new information and therefore only reproduces the positive frequency range. The second relation known as **Kramers-Kronig** relation shows, that real- and imaginary part of the susceptibility are linked with each other, and even that one follows from the other. For example, the real part of the equation above allows a derivation of the real part of the susceptibility from the imaginary part

$$\text{Re} [\chi(\omega)] = \frac{1}{\pi} P \int_{-\infty}^{\infty} d\bar{\omega} \frac{\text{Im} [\chi(\bar{\omega})]}{\bar{\omega} - \omega},$$

that means absorptive processes ($\text{Im} [\chi(\bar{\omega})]$) are closely linked to the refractive ones ($\text{Re} [\chi(\omega)]$). A nonvanishing susceptibility always has a real- and an imaginary part, thus is a complex function of the frequency.

Derivation of the **Kramers Kronig** relation

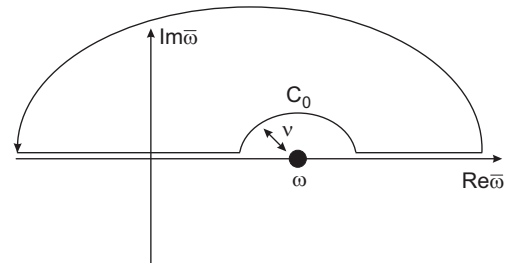
(not represented in the lecture and not subject of any exercises)

point of departure

- $\chi(\omega) = \int_{-\infty}^{+\infty} d\tau R(\tau) e^{i\omega\tau}$
- $R(\tau < 0) = 0$ and R remains finite for all positive τ
 $\Rightarrow \chi(\omega)$ is analytic in the upper complex plane with respect to ω
- χ must decay for large ω as the response function decays exponentially for large τ ($R(\tau) \sim e^{-\gamma\tau}$ for $\tau \rightarrow +\infty$) $\chi(\omega)$ decays indeed as $\frac{1}{|\omega|}$

performing an integral on a closed loop

- the function $\frac{\chi(\bar{\omega})}{\bar{\omega} - \omega}$ is integrated along a closed contour C with respect to $\bar{\omega}$
- the contour C contains
 - a long integration along the real axis from $-\infty$ to $\omega - \nu$
 - a small semicircle C_0 with radius ν to avoid the divergence at $\bar{\omega} = \omega$
 - a long integration along the real axis from $\omega + \nu$ to $+\infty$
 - an infinite semicircle C_∞ from $+\infty$ to $-\infty$ to close the loop
- as the integrand is analytic in the upper half plane the whole integral vanishes $\oint_C d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega} - \omega} = 0$



limiting case $\nu \Rightarrow 0$

$$0 = \lim_{\nu \rightarrow 0} \oint_C d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega} - \omega} = \lim_{\nu \rightarrow 0} \left[\int_{-\infty}^{\omega - \nu} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega} - \omega} + \int_{-\omega + \nu}^{+\infty} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega} - \omega} + \int_{C_\infty} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega} - \omega} + \int_{C_0} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega} - \omega} \right]$$

discussion of the individual terms

- $\int_{C_0} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega} - \omega}$ vanishes as the integrand decays like $\frac{1}{\bar{\omega}^2}$ for diverging radius of integration

- $\lim_{\nu \rightarrow 0} \int_{C_\infty} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega} - \omega}$: For vanishing radius ν the susceptibility $\chi(\bar{\omega})$ can be assumed to be constant on the contour

$$\lim_{\nu \rightarrow 0} \int_{C_\infty} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega} - \omega} = \chi(\omega) \lim_{\nu \rightarrow 0} \int_{C_0} d\bar{\omega} \frac{1}{\bar{\omega} - \omega} = \chi(\omega) \int_{\pi}^0 d\varphi \frac{\nu i e^{i\varphi}}{\nu e^{i\varphi}} = -i\pi \chi(\omega),$$

where we have used $\bar{\omega} - \omega = \nu e^{ip}$ $d\bar{\omega} = \nu i e^{i\varphi} d\varphi$

Hence the Kramers-Kronig relation as displayed on page 20 follows as

$$\chi(\omega) = \frac{1}{i\pi} \lim_{\nu \rightarrow 0} \left[\int_{-\infty}^{\omega - \nu} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega} - \omega} + \int_{\omega + \nu}^{+\infty} d\bar{\omega} \frac{\chi(\bar{\omega})}{\bar{\omega} - \omega} \right]$$

4 Basic concepts of quantum mechanics

4.1 Fundamental experiments on quantum phenomenas

4.1.1 Experiments on the particle character of light

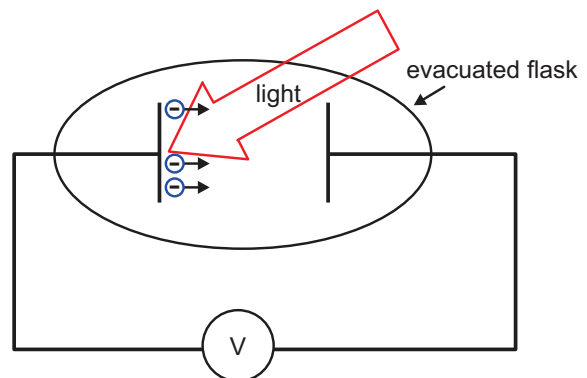
Photoelectric effect

Observations (Hertz 1887, Hallwachs 1895)

- negative charged metal plates discharge when exposed to light of a certain wavelength.
- positive charged metal plates do not discharge. $\Rightarrow e^-$ discharging by the emission of electrons
- there is no discharge if the wavelength of the light is above a certain border wavelength.
- Discharge starts immediately.

Quantitative measurement (Lenard 1902)

An electrode inside an evacuated flask is irradiated with monochromatic light. Due to emission of electrons a countervoltage between both electrodes builds up, that converges towards a static value U_0 . In the static case (with the current died out) the energy of the emitted electrons is just no longer sufficient to overcome



the potential difference between the two electrodes. Therefore the observed current is a measure of the kinetic energy of the emitted electrons. $E_{\text{kin}} = eU_0$

If the the current flowing throug the voltmeter is negligible then the corresponding counter-voltage arises after a short time. If no voltmeter with high resistance is available, an external voltage can be attached and the voltage parameter, that just suppresses any current flow, has to be determined with the help of an amperemeter.

Essential results

- the kinetic energy of the electrons depends linear on the frequency of light, but not on the intensity.
- There is no longer an emission of electrons below a certain frequency of the incident light.
- No measurable delay exists between the beginning of the exposure and the beginning of the electron emission.

Kinetic energy of electrons in the classical theory

$$E_{\text{kin}} \leq \frac{\text{Intensity} \cdot \text{time}}{\text{penetration depth} \cdot \text{electron density}} - \text{work function}$$

← deposited energy
← irradiated volume

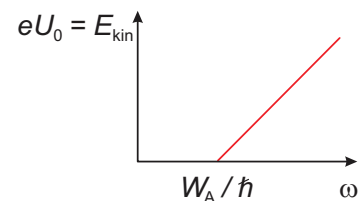
The kinetic energy of electrons should depend strongly on the intensity and comparatively weak (only by the penetration depth) on the frequency. Even if it is assumed, that the total optical energy is absorbed within the first atomic layer, the kinetic energy of the electrons would first reach positive values after days and thus permit an immediate emission.

Light quantum hypothesis (Einstein 1905)

- Emission and absorption of light occurs only in form of complete light quanta – so called photons.
- Any photon has a definite energy $E = hf = \hbar\omega$, determined by the frequency f with Planck's constant $h = 6.6261 \times 10^{-34}$ Js or $\hbar = h/2\pi$.

Explanation of the experiment

- For $\hbar\omega < W_A$ (W_A : work function) no emission is possible.
- The kinetic energy of the emitted electrons is $E_{\text{kin}} = \hbar\omega - W_A$
- The emission of electrons occurs instantly, since photons are absorbed immediately.



one photon \rightarrow one emitted electron

Compton scattering

Setup of the experiment (Compton 1922)



quasi-free electrons: weak coupled shell electrons (the work function is far smaller than the energy of the γ -ray quanta)

Observation

Frequency shift of scattered radiation, depending on the scattering angle φ .

Interpretation

A photon of the energy $E_0 = hf_0$ collides with a stationary electron. The acceleration of the electron leads to a reduction of the energy of the photon and as a result to a redshift.

Conclusion

Since the electron receives momentum, the photon must have momentum too. Only two vectors are associated with the propagation of light: the wave vector \vec{k} and the Poynting vector \vec{s} . But both vectors are parallel in vacuum and in isotropic media. Therefore, the momentum of a photon can only be directed in direction of the wave vector \vec{k} .

speculation: $\vec{p} = \hbar\vec{k}$

Quantitative analysis

Since the scattered electrons can be accelerated to considerable velocities, relativistic calculus is necessary

1. relativistic momentum:

$$\vec{p} = m(\nu)\vec{u} = \frac{m_0}{\sqrt{1 - \nu^2/c^2}}\vec{v}$$

with

velocity: $\vec{\nu}$ and $\nu = |\vec{\nu}|$

speed of light: c

relativistic masses: $m(\nu)$

rest mass: m_0

Note: The "relativistic mass" is quite useful to memorize some relations of special relativity. However, in the general calculus it is not used as it is not invariant.

2. relativistic energy

$$E = \sqrt{m_0^2 c^4 + \vec{p}^2 c^2} = m(\nu) c^2 = \frac{m_0}{\sqrt{1 - \nu^2/c^2}} c^2$$

For low velocities ($\nu \ll c$) the energy can be expanded with respect to powers of \vec{p}^2

$$E \approx m_0 c^2 + \frac{\vec{p}^2}{2m_0} + \dots$$

So, the rest energy results as $m_0 c^2$

3. energy balance of the collision

$$hf_0 = hf_s + E_{\text{kin}}$$

with the frequencies of the γ -rays before (ω_0) and after (ω_s) the collision.

4. momentum balance of the collision

$$\hbar \vec{k}_0 = \hbar \vec{k}_s + \vec{p}_e$$

with the momentum of the electron \vec{p}_e and with the wave vectors of the γ -ray before (\vec{k}_0) and after (\vec{k}_s) the collision.

By utilizing the fact, that the scattering angle φ equals the angle between \vec{k}_0 and \vec{k}_s and that $|\vec{k}_{0/S}| = \frac{2\pi}{c} f_{0/S}$ applies, \vec{p}_e^2 can be expressed via the momentum balance by

$$\vec{p}_e^2 = \frac{h^2}{c^2} (f_0^2 + f_s^2 - 2f_0 f_s \cos \varphi)$$

and via the energy balance by

$$\vec{p}_e^2 = \frac{h^2}{c^2} (f_0^2 + f_s^2 - 2f_0 f_s) + 2hm_0(f_0 - f_s)$$

Equating both terms, we find by using $\lambda_{0/S} = c/f_{0/S}$ that the wavelength shift is

$$\lambda_S - \lambda_0 = \lambda_C(1 - \cos \varphi)$$

with the Compton-wavelength

$$\lambda_C = \frac{h}{m_0 c}$$

For electrons, a Compton-wavelength of $\lambda_C = 2.4 \times 10^{-12}$ m appears, i.e. the Compton-effect can be observed in the hard γ -ray range only.

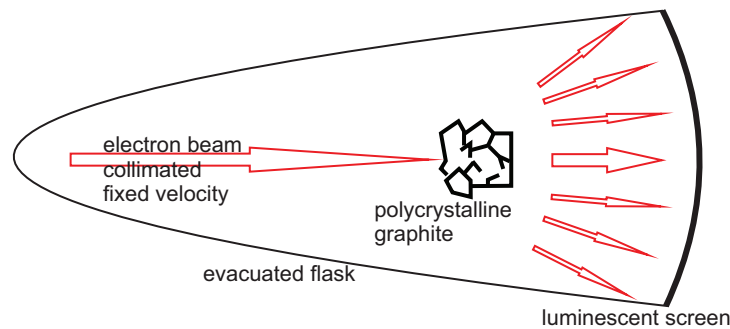
Since the results of the derivation above show good agreement with the experiment, we can be sure, that light, when interacting with matter, behaves like a particle with the energy $E = \hbar\omega$ and the momentum $\vec{p} = \hbar\vec{k}$.

4.1.2 Experiments on the wave character of particles

The wave nature of a phenomenon becomes apparent, as soon as interference occurs if multiple optical paths are superimposed.

Electron diffraction on graphite crystals

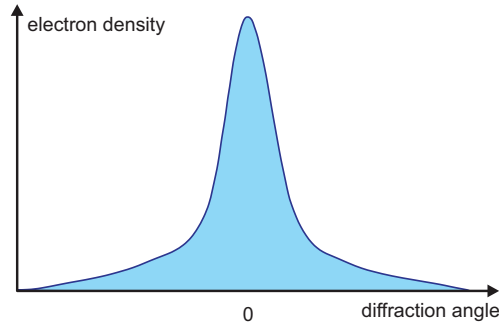
setup



expected results for scattering of classical particles

Since the interaction is relative weak, each electron, which is scattered is diffracted by only one individual atom. Therefore the scattering on the crystal is a sum of individual scattering events, that all happen in the same manner. Thus the same distribution that also would be found for multiple scattering on a single atom should be detected on the screen. But the scattering on a single atom is a function decreasing monotoneously with the scattering angle. So, we expect

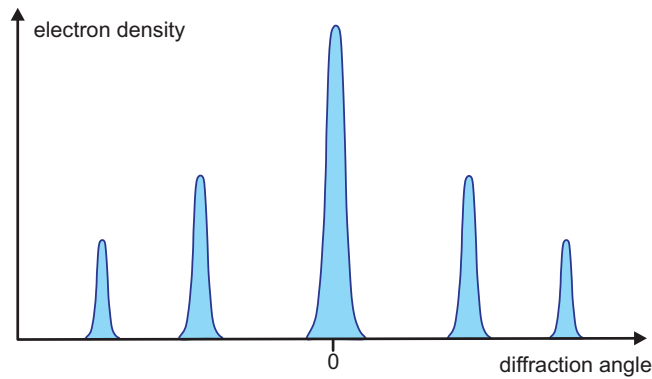
to find a high electron density in the center of the screen, and an electron distribution, which quickly decreases with growing angles.



Scattering distribution according to a "classical" theory

distribution observed in the experiment

In the experiment, a significant stronger structured circular scattering distribution is observed. The appearance of explicit minima indicates the occurrence of interference effects. The electron does not behave like a "classical particle" but rather like a wave, diffracted on the graphite. In fact, very similar diffraction pattern can be generated with γ -ray.



Scattering distribution observed in the experiment

4.2 Consequences of the wave nature of the electron

1. wavelength of an electron

Since the motion of an electron is described by only one vector, the momentum, the wave vector of the corresponding particle wave must be related to it. The relation $\vec{p} = \hbar \vec{k}$, already known for photons, is adopted. If the electron has a certain kinetic energy E_{kin} , that it got for example by passing a current $U(E_{\text{kin}} = eU)$, then the absolute value of the momentum p , and thus the wavelength λ_e , results from it. In the relativistic case, the kinetic energy is the difference between

total energy and rest energy

$$E_{\text{kin}} = \sqrt{m_0^2 c^4 + c^2 p^2} - m_0 c^2,$$

where the absolute value of the momentum results as

$$p = \sqrt{2m_0 E_{\text{kin}} + E_{\text{kin}}^2 / c^2},$$

where the second term in the root is the relativistic correction. Now, the wavelength is given by

$$\lambda_e = \frac{2\pi}{|k|} = \frac{2\pi\hbar}{p} = \frac{h}{\sqrt{2m_0 E_{\text{kin}} + E_{\text{kin}}^2 / c^2}}.$$

But as long as the kinetic energy of an electron is significantly lower than its rest energy (rest energy of an electron: 512 keV), nonrelativistic calculus with the classical formula for kinetic energy $E_{\text{kin}} \approx \frac{p^2}{2m_0}$ can be used. In that case the wavelength can be determined by $\lambda_e = \frac{h}{\sqrt{2m_0 E_{\text{kin}}}}$. For an electron mass of $m_0 = 9.109 \times 10^{-31}$ kg and a kinetic energy of 1 eV a wavelength of $\lambda_e = 1.2$ nm results.

2. limits of the classical behavior

For a classical particle, a well-defined place and a likewise accurately determined momentum are assumed, i.e. the particle follows a trajectory precisely determined in position and direction. With that, the image of ray optics is reproduced, where light also gets assigned an exact position, as well as a proper defined direction. However, the concept of ray optic collapses, as soon as a spatial resolution in the range of the wavelength shall be achieved. Analogue, we can assume classical behavior for particles, as long as we do not deal with spatial dimensions that match the range of the respective wavelength of the particle $\lambda_e = h/\sqrt{2m_0 E_{\text{kin}}}$. Hence, heavy or energetic particles behave much more "classical". If one is interested in quantum behavior in macroscopic dimensions, like the production of Bose-condensates, the kinetic energy of the involved particles has to be suitable reduced, i.e. especially their temperature has to be decreased.

4.3 Governing equations of quantum mechanics

4.3.1 Schrödinger-equation (Schrödinger 1926)

starting point:

- description of particle dynamics by a complex wave function $\Psi(\vec{r}, t)$
- probability to find a particle in a certain place $\rho(\vec{r}, t) = |\Psi(\vec{r}, t)|^2$

- A spatial dependence of $\Psi(\vec{r}, t)$ of the form $e^{i\vec{k}\vec{r}}$ represents a particle with the momentum $\vec{p} = \hbar\vec{k}$
- A temporal dependency of $\Psi(\vec{r}, t)$ of the form $e^{-i\omega t}$ represents a particle with the energy $E = \hbar\omega$

We want to find:

An equation of motion for $\Psi(\vec{r}, t)$, that converges to Newtonian's equations for high energies and high momenta.

We formulate an equation of motion

a) Spatial dependence

By applying the gradient to an arbitrary wave function Ψ , the momentum can be found

$$\frac{\hbar}{i}\nabla\Psi(\vec{r}, t) = \vec{p}\Psi(\vec{r}, t)$$

$$\text{proof}^1: \frac{\hbar}{i}\nabla e^{i\vec{k}\vec{r}} = \hbar\vec{k}e^{i\vec{k}\vec{r}} = \vec{p}e^{i\vec{k}\vec{r}}$$

b) temporal dependence

Analogue to a) we apply a differentiation with respect to t

$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t) = E\Psi(\vec{r}, t)$ keeping in mind that a wave with the time dependence $\sim \exp(-i\omega t)$ carries quanta with the energy $\hbar\omega$

c) (non relativistic) expression of the energy

$$\begin{aligned} E &= \frac{\vec{p}^2}{2m} + V(\vec{r}) \\ i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t) &= \left[\frac{\vec{p}^2}{2m} + v(\vec{r}) \right] \Psi(\vec{r}, t) \\ \vec{p} &= \frac{\hbar}{i}\nabla \\ \vec{p}^2 &= -\hbar^2\nabla^2 = -\hbar^2 \left[\vec{e}_x \frac{\partial}{\partial x} + \vec{e}_y \frac{\partial}{\partial y} + \vec{e}_z \frac{\partial}{\partial z} \right]^2 \\ &= -\hbar^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\hbar^2\nabla^2 \end{aligned}$$

With that, the Schrödinger-equation results as

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t) = \left[-\frac{\hbar^2}{2m}\Delta + V(\vec{r}) \right] \Psi(\vec{r}, t)$$

$\Psi(\vec{r}, t) \Rightarrow$ physical quantities:

¹Because it works for all plane waves, it has to apply to any Ψ since plane waves are complete.

1. Usually this equation is normalized. Because the probability to observe a single particle at all is unity

$$\int d^3r |\Psi(\vec{r}, t)|^2 = \int d^3r \rho(\vec{r}, t) = 1$$

2. If $\Psi(\vec{r}, t)$ is known, the question arises, how to obtain predictions for experimental data. For example, one possibility is the mean position, i.e. the place where the particle can be found in the average.

$$\langle \vec{r} \rangle = \frac{\int d^3r \rho(\vec{r}, t) \vec{r}}{\int d^3r \rho(\vec{r}, t)}$$

3. For the mean momentum we have

$$\langle \vec{p} \rangle = \frac{\int d^3r \Psi^*(\vec{r}, t) \frac{\hbar}{i} \nabla \Psi(\vec{r}, t)}{\int d^3r \Psi^* \Psi}$$

4. In general any experimentally observable quantity A we can attribute to an operator \hat{A}

$$\begin{aligned} \vec{r} &\Rightarrow \vec{r} \\ \vec{p} &\Rightarrow \frac{\hbar}{i} \nabla \end{aligned}$$

The mean experimentally observed value of A is

$$\langle A \rangle = \int d^3r \Psi^* \hat{A} \Psi$$

4.3.2 States of fixed energy – the time independent Schrödinger equation

For many phenomena, the energy is well defined and conserved. Examples are the energy levels in atoms. In this case we can set

$$\begin{aligned} \Rightarrow E_0 &= \text{const.} \\ \Rightarrow \text{fixed time dependency} &\sim e^{-i\omega_0 t} \end{aligned}$$

Note that there is neither a fixed zero point energy nor an absolute temporal dynamics. Only the probability density $|\Psi|^2$ is important, which means, that

- \Rightarrow the absolute frequency is unimportant
- \Rightarrow the temporal dynamics is only determined by interference terms and frequency differences $\Delta\omega$
- \Rightarrow only energy differences are important

Thus we can remove the time dependence as we already did for monochromatic fields like full time dependence Ψ

$\Psi(\vec{r}, t) = \psi(\vec{r}) \exp(-i\omega_0 t)$ only space dependence Ψ

Thus the time independent Schrödinger equation can be formulated as

$$E_0 \psi = \left[-\frac{\hbar^2}{2m} \Delta + V(\vec{r}) \right] \psi$$

with $E_0 = \hbar\omega_0$

formal notation

$\hat{H}\psi = E\psi$ (\hat{H} - Hamilton operator, E - eigenvalue)

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V$$

finding the right energies $\hat{=}$ eigenvalue problem \Rightarrow not every E is allowed / is an eigenvalue!

4.3.3 Simple solutions of the time-independent Schrödinger equation

a) free particle

Free particles are particles in the absence of a potential $V(\vec{r}) = V_0 = \text{constant}$. The time independent Schrödinger equation now reads as

$$(E_0 - V_0) \frac{2m}{\hbar^2} \psi + \Delta \psi = 0.$$

It is equal to the Helmholtz equation for monochromatic light provided that $E_0 > V_0$ holds. We can immediately transfer respective solutions and obtain that

- free particles are found for all energies $E_0 > V_0$ (continuous spectrum) and
- have a wave function $\psi(\vec{r}) = \psi_0 \exp(i\vec{k}\vec{r})$
- with the dispersion relation $\vec{k}^2 = (E_0 - V_0) \frac{2m}{\hbar^2}$

b) box potential \Rightarrow www.st-andrews.ac.uk/physics/quvis

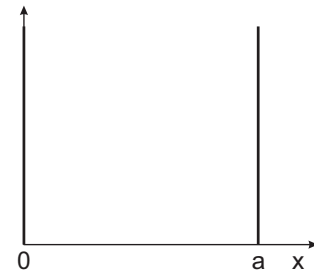
the box potential consists of a flat bottom with constant potential $V(\vec{r}) = V_0 = \text{constant}$, which we set to zero $V_0 = 0$. This bottom is surrounded by infinite walls, where the potential is infinity.

In the one-dimensional case this reads as:

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < a \\ +\infty & \text{for } x < 0 \text{ or } x > a \end{cases}$$

This is the simplest potential one can imagine. Still it is a good approximation for electrons in quantum wells and in the 3d-case for nuclear particles inside a nucleus. In the 2d-case the time independent Schrödinger equation reads as

$$E_0\psi = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi$$



We now try to find a solution for the wave function

Outside of the potential: $x < 0$ and $x > a$

$\psi(x) = 0$ since a finite $|\psi(x)|^2$ causes a diverging potential energy.

Inside the potential: $0 < x < a$, $V = 0$

$$\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi + E_0\psi = 0$$

with the solution

$$\psi = A_+ e^{i\kappa x} + A_- e^{-i\kappa x} \quad \text{mit} \quad \kappa = \frac{1}{\hbar} \sqrt{2mE_0}$$

boundary conditions at $x = 0$: $A_+ + A_- = 0$ ²

$$\psi = \psi_0 \sin(\kappa x)$$

boundary conditions at $x = a$

$$\sin(\kappa a) = 0$$

$$\rightarrow \kappa \cdot a = n \cdot \pi \quad n = 1, 2, \dots$$

$$\rightarrow \kappa = n \frac{\pi}{a}$$

$$\begin{aligned} \frac{1}{\hbar} \sqrt{2mE_n} &= n \frac{\pi}{a} \\ E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2} &= n^2 \frac{\hbar^2}{8ma^2} \end{aligned}$$

In contrast to the free particle we find

- discrete energies (discrete spectrum)
- a ground state ($n = 1$), which already has a finite energy different from V_0

²the same momentum applies for forward direction and reverse direction, in the quantum mechanic mean, the particle is at rest.

It is interesting to look for the mean momentum of the different states

$$\langle p \rangle = \int_0^a dx \Psi^* \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi = \int_0^a dx \psi^* \frac{\hbar}{i} \frac{\partial}{\partial x} \psi$$

As ψ is real we get

$$\langle p \rangle = \int_0^a dx \psi \frac{\hbar}{i} \frac{\partial}{\partial x} \psi = \frac{\hbar}{2i} \int_0^a dx \frac{\partial}{\partial x} \psi^2 = \frac{\hbar}{2i} [\psi(a)^2 - \psi(0)^2] = 0$$

Hence, the particle in an eigenstate is at rest no matter how much energy it has.

the momentum distribution

momentum (1D): $P = \hbar k \Rightarrow$ Fourier transformation

$$\psi(p) = \underbrace{\frac{1}{\sqrt{2\pi\hbar}}}_{\text{normalisation}} \underbrace{\int_0^a dx \psi(x) e^{-i\frac{p}{\hbar}x}}_{\sim \text{normalisation}}$$

state n

$$\begin{aligned} \psi(p) &= \frac{1}{\sqrt{2\pi\hbar}} \int_0^a dx \psi_0 \sin\left(n\frac{\pi}{a}x\right) e^{-i\frac{p}{\hbar}x} \\ &= \frac{\psi_0}{\sqrt{2\pi\hbar}} \frac{(-1)}{2} \frac{1}{\left[n\frac{\pi}{a} - \frac{p}{\hbar}\right]} \left[e^{i\left(n\frac{\pi}{a} - \frac{p}{\hbar}\right)a} - 1 \right] + \frac{\left[e^{-i\left[n\frac{\pi}{a} - \frac{p}{\hbar}\right]a} - 1 \right]}{\left[n\frac{\pi}{a} + \frac{p}{\hbar}\right]} \end{aligned}$$

dynamical effects

general wavefunction at $t = 0$

$\Psi(x, t = 0) = \sum_{n=1}^{\infty} a_n \psi_n(x)$ (Ψ - evolution, $\psi_n(x)$: complete set of functions)

$$\Psi(x, t) = \sum_{n=1}^{\infty} a_n \psi_n(x) e^{-i\frac{E_n}{\hbar}t}$$

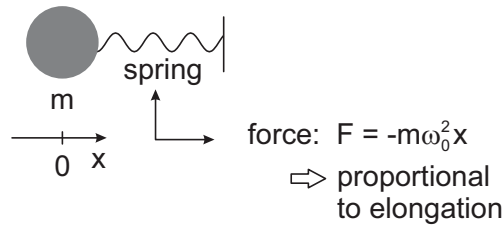
$$\Psi(x, t) = \sum_{n=1}^{\infty} a_n \psi_n(x) e^{in^2 \frac{\hbar}{8ma^2}t}$$

periodic recovery of every initial distribution after a period T with

$$\begin{aligned} \frac{\hbar}{8ma^2}T &= p \cdot 2\pi & p : \text{integer} \\ T &= p \cdot \frac{8ma^2}{\hbar} \end{aligned}$$

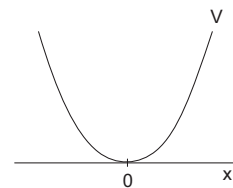
4.3.4 Harmonic oscillator (1D)

system



potential: $V(x) = \frac{1}{2}m\omega_0^2 x^2$

with $\frac{\partial V}{\partial x} = -F$

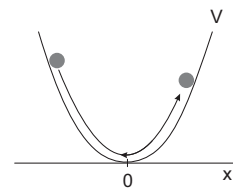


classical evolution equation

$$\underbrace{m\ddot{x}}_{\text{inertia}} = F = -m\omega_0^2 x$$

$$\Rightarrow \ddot{x} + \omega_0^2 x = 0$$

$$\Rightarrow \text{solution: } x(t) = x_0 e^{-i\omega_0 t} + x_0^* e^{i\omega_0 t}$$



quantum mechanical formulation

particle has no fixed position x , but a probability distribution $|\Psi(x, t)|^2$

dynamics of Ψ : Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi + \underbrace{\frac{1}{2}m\omega_0^2 x^2}_{V(x)} \Psi$$

Looking for eigenstates with fixed energy E

$$E\psi(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi + \frac{1}{2}m\omega_0^2 x^2 \psi$$

$$\frac{\partial^2}{\partial x^2} \psi - \left[\frac{m\omega_0}{\hbar} \right]^2 x^2 \psi + \frac{2mE}{\hbar^2} \psi = 0$$

1. find a guess

$$x \rightarrow \infty \Rightarrow \frac{2mE}{\hbar^2} \ll \left[\frac{m\omega_0}{\hbar} \right]^2 x^2$$

approximate solution for

$$\begin{aligned}
\frac{\partial^2}{\partial x^2} \psi_\infty - \left[\frac{m\omega_0}{\hbar} \right]^2 x^2 \psi_\infty &= 0 \\
\psi_\infty &\approx e^{-\alpha x^2} \\
\frac{\partial \psi_\infty}{\partial x} &= -2\alpha x \psi_\infty \\
\frac{\partial^2 \psi_\infty}{\partial x^2} &= [-2\alpha + 4\alpha^2 x^2] \psi_\infty \\
\frac{\partial^2}{\partial x^2} \psi_\infty - \left[\frac{m\omega_0}{\hbar} \right]^2 x^2 \psi_\infty &= \left[-2\alpha + 4\alpha^2 x^2 - \left[\frac{m\omega_0}{\hbar} \right]^2 x^2 \right] \psi_\infty \\
x \rightarrow \infty &\approx \left[4\alpha^2 - \left[\frac{m\omega_0}{\hbar} \right]^2 \right] x^2 \psi_\infty
\end{aligned}$$

$$\begin{aligned}
\Rightarrow \alpha &= \frac{m\omega_0}{2\hbar} \\
\psi_\infty &= e^{-\frac{m\omega_0}{2\hbar} x^2}
\end{aligned}$$

2. find a first solution

insert ψ_∞ into the original equation $\psi' = \psi_0 \psi_\infty$

$$\frac{\partial^2}{\partial x^2} \psi - \left[\frac{m\omega_0}{\hbar} \right]^2 x^2 \psi + \frac{2mE}{\hbar^2} \psi = \left[-2\alpha + \frac{2mE}{\hbar^2} \right] \psi_0 \psi_\infty \stackrel{!}{=} 0$$

for

$$\alpha = \frac{mE}{\hbar^2} \Rightarrow E = \frac{\hbar^2}{m} \alpha = \frac{\hbar^2}{m} \frac{m\omega_0}{2\hbar}$$

$\psi = \psi_0 e^{-\frac{m\omega_0}{2\hbar} x^2}$ is a solution for $E = \frac{\hbar\omega_0}{2}$

ψ_0 : determined by normalization $\int dx |\psi|^2 = 1$

$$\psi_0 = \sqrt[4]{\frac{m\omega_0}{\hbar\pi}}$$

3. ground state solution

$$\psi_0 = \sqrt[4]{\frac{m\omega_0}{\hbar\pi}} e^{-\frac{m\omega_0}{2\hbar} x^2} \quad \text{with energy} \quad E_0 = \frac{\hbar\omega_0}{2}$$

4. further solutions

general ansatz

$$\psi = \sum_{n=0}^{\infty} a_n x^n e^{-\alpha x^2}$$

\Rightarrow includes the ground state solution

\Rightarrow complete set of functions

$$\begin{aligned}
\frac{\partial}{\partial x}\psi &= \sum_{n=0}^{\infty} a_n [nx^{n-1} - 2\alpha x^{n+1}] e^{-\alpha x^2} \\
\frac{\partial^2}{\partial x^2}\psi &= \sum_{n=0}^{\infty} a_n [n(n-1)x^{n-2} - 4n\alpha x^n - 2\alpha x^n + 4\alpha^2 x^{n+2}] e^{-\alpha x^2} \\
\frac{\partial^2}{\partial x^2} - \left[\frac{m\omega_0}{\hbar}\right]^2 x^2 + \left[\frac{2mE}{\hbar^2}\right]\psi &= \sum_{n=0}^{\infty} \left[a_{n+2}(n+2)(n+1) - 2(2n+1)\alpha a_n + \right. \\
&\quad \left. + 4\alpha^2 a_{n-2} - \left[\frac{m\omega_0}{\hbar}\right]^2 a_{n-2} + \frac{2mE}{\hbar^2} a_n \right] x^n e^{-\alpha x^2}
\end{aligned}$$

$\stackrel{!}{=} 0 \Rightarrow$ should be true for each component of the sum

$$\begin{aligned}
(n+2)(n+1)a_{n+2} - \left[2(2n+1)\frac{m\omega_0}{2\hbar} - \frac{2mE}{\hbar^2} \right] a_n + \left[4\frac{m^2\omega_0^2}{4\hbar^2} - \frac{m^2\omega_0^2}{\hbar^2} \right] a_{n-2} &= 0 \\
\Rightarrow a_{n+2} = \frac{1}{(n+1)(n+2)} \frac{2m}{\hbar^2} \left[\left(n + \frac{1}{2} \right) \hbar\omega_0 - E \right] a_n
\end{aligned}$$

approximation of recursion formula for large n

$$\begin{aligned}
a_{n+2} &\approx \frac{1}{n+2} \frac{2m\omega_0}{\hbar} a_n \\
\Rightarrow a_{2K} &\approx \frac{1}{K!} \left[\frac{m\omega_0}{\hbar} \right]^K a_0 & a_{2K+1} &\approx \frac{1}{K!} \left[\frac{m\omega_0}{\hbar} \right]^K a_1 \\
\Rightarrow \sum_{n=0}^{\infty} a_n x^n &\approx a_0 \sum_{K=0}^{\infty} \frac{1}{K!} \left[\frac{m\omega_0}{\hbar} x^2 \right]^K + a_1 x \sum_{K=0}^{\infty} \frac{1}{K!} \left[\frac{m\omega_0}{\hbar} x^2 \right]^K \\
&\approx [a_0 + a_1 x] \exp \left[\frac{m\omega_0}{\hbar} x^2 \right] \\
\psi(x) &= \sum_{n=0}^{\infty} a_n x^n \exp \left[-\frac{m\omega_0}{2\hbar} x^2 \right] \\
\psi(x) &= [a_0 + a_1 x] e^{\frac{m\omega_0}{2\hbar} x^2}
\end{aligned}$$

$\Rightarrow \psi(x)$ is diverging for large x

\Rightarrow recursion formula must terminate!

$\Rightarrow E = E_n = \left(n + \frac{1}{2} \right) \hbar\omega_0$ and

$$\psi(x) = \underbrace{\sum_{n'=0}^n a_{n'} x^{n'}}_{\text{finite polynomial}} e^{-\frac{m\omega_0}{2\hbar} x^2}$$

general solution

$$\psi_n(x) = \underbrace{\sqrt{\frac{m\omega_0}{\pi\hbar}} \frac{1}{\sqrt{2^n n!}}}_{\text{normalization}} \underbrace{H_n\left(\sqrt{\frac{m\omega_0}{\hbar}}x\right) e^{-\frac{m\omega_0}{2\hbar}x^2}}_{\text{finite polynomial}}$$

H_n : Hermite-polynomials

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} [e^{-x^2}]$$

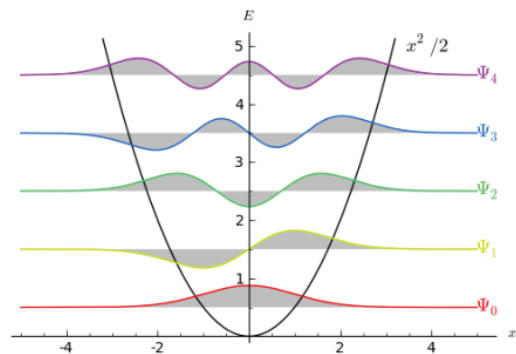
$$H_0(x) = 1$$

$$H_1(x) = 2x$$

$$H_2(x) = 4x^2 - 2$$

main results for the harmonic oscillator

- discrete energy spectrum $E_n = (n + \frac{1}{2}) \hbar\omega_0$ with equidistant spacing
- finite zero point energy $\frac{1}{2}\hbar\omega_0$



4.3.5 Operator relations

physical observable $A \hat{=}$ hermitian operator \hat{A}

measurement $\hat{=}$ application of \hat{A} on ψ

quantum mechanics: a measurement may influence the system

\Rightarrow the order of measurements can matter

$\Rightarrow \hat{A}\hat{B}|\psi\rangle$ usually not equal $\hat{B}\hat{A}|\psi\rangle$

quantification of this property: commutator $[\hat{A}\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

order of measurements does not matter $[\hat{A}\hat{B}] = 0$

\hat{A} and \hat{B} have a common complete system of eigenfunctions $|\psi_n\rangle$ with $\hat{A}|\psi_n\rangle = a_n|\psi_n\rangle$ and

$\hat{B}|\psi_n\rangle = b_n|\psi_n\rangle$

prominent example: position and momentum

$$\begin{aligned} [\hat{x}, \hat{p}_x] |\psi\rangle &= x \frac{\hbar}{i} \frac{\partial}{\partial x} \psi - \frac{\hbar}{i} \frac{\partial}{\partial x} [x\psi] \\ &= x \frac{\hbar}{i} \frac{\partial}{\partial x} \psi - \frac{\hbar}{i} \psi - x \frac{\hbar}{i} \frac{\partial}{\partial x} \psi = i\hbar \psi \end{aligned}$$

$$\Rightarrow [\hat{x}, \hat{p}_x] = i\hbar \text{ or } [x_i, p_j] = i\hbar \delta_{ij}$$

5 The hydrogen atom and beyond

5.1 Angular momentum operators electron in coulomb-potential of the proton

⇒ system of spherical symmetry

⇒ angular momentum conserved

classical: $\vec{L} = \vec{r} \times \vec{p}$

quantum: $\hat{\vec{L}} = \hat{\vec{r}} \times \frac{\hbar}{i} \nabla$ commutator relations

e.g. $\hat{L}_x = \frac{\hbar}{i} \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right]$

$$\begin{aligned} [L_x, L_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \\ &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\ &= \hat{y} [\hat{p}_z, \hat{z}] \hat{p}_x + \hat{x} [\hat{z}, \hat{p}_y] \hat{p}_z \\ &\quad \underbrace{-i\hbar} \quad \underbrace{i\hbar} \\ &= i\hbar [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x] = i\hbar L_z \end{aligned}$$

analog

$$[L_y, L_z] = i\hbar L_x \text{ and } [\hat{L}_z, \hat{L}_x] = i\hbar L_y \text{ (zyclic permutation)}$$

absolute value of the angular momentum

$$\hat{\vec{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \text{ with } [\hat{L}_i, \hat{\vec{L}}^2] = 0$$

⇒ joint eigenfunctions for \hat{L}_z and $\hat{\vec{L}}^2$

optimum coordinates for problems with spherical symmetry:

spherical coordinates: r, θ, φ

$\hat{\vec{L}}^2$ in spherical coordinates

$$\hat{\vec{L}}^2 = -\hbar^2 \Delta_{\theta\phi}$$

$$\text{with } \Delta_{\theta,\phi} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \right] + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

5.2 Particles in a spherical potential

a) quantum numbers

time independent Schrödinger equation

$$\hat{H}\psi(\vec{r}) = \left[-\frac{\hbar^2}{2m} \Delta + V(r) \right] \psi(\vec{r}) = E\psi(\vec{r})$$

depends on $r = \sqrt{x^2 + y^2 + z^2} = |\vec{r}|$ only

Δ in spherical coordinates

$$\Delta = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \Delta_{\theta\phi} \quad \hat{H} = -\frac{\hbar^2}{2m} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2} \right\} + V(r)$$

$$\Rightarrow \left. \begin{aligned} [\hat{H}, \hat{L}^2] &= 0 \\ [\hat{L}^2, \hat{L}_z] &= 0 \\ [\hat{H}, \hat{L}_z] &= 0 \end{aligned} \right\} \hat{H}, \hat{L}^2 \text{ and } \hat{L}_z \text{ posses a joint eigenfunction systems}$$

Eigenfunctions of a Hamiltonian with a potentials with spherical symmetry have fixed total angular momentum (eigenvalue of \hat{L}^2) and a fixed z -component of the angular momentum (eigenvalue of \hat{L}_z).

\Rightarrow 3 quantum numbers corresponding to eigenvalues of \hat{H} , \hat{L}^2 and \hat{L}_z

b) separation of variables

ansatz: $\psi(r, \theta, \phi) \stackrel{!}{=} R(r)Y(\theta, \phi)$

$$\underbrace{-\frac{\hbar^2}{2m} \frac{\partial}{\partial r} \left[r^2 \frac{\partial}{\partial r} RY \right] - \frac{\hbar^2}{2m} \Delta_{\theta\phi} RY + r^2 [V(r) - E] RY}_{f(r)} = \underbrace{-\frac{1}{R(r)} \frac{\partial}{\partial r} \left[r^2 \frac{\partial}{\partial r} R \right] - \frac{2m}{\hbar^2} r^2 [V(r) - E]}_{g(\theta, \phi)} = -\frac{1}{y(\theta, \phi)} \Delta_{\theta\phi} Y$$

$$\frac{\partial f}{\partial r} = \frac{\partial g(\theta, \phi)}{\partial r} = 0 \quad \Rightarrow f = -\lambda_1 \quad (\lambda_1: \text{unknown constant})$$

2 separate equations:

$$-\frac{\lambda_1}{r^2} R(r) + \frac{1}{r^2} \frac{\partial}{\partial r} [r^2 R(r)] + \frac{2m}{\hbar^2} (E - V(r)) R(r) = 0$$

$$\underbrace{-\hbar^2 \Delta_{\theta\phi} Y(\theta, \phi)}_{\hat{L}^2} = \underbrace{\lambda_1 \hbar^2 Y(\theta, \phi)}_{\text{eigenvalue}}$$

$\Rightarrow \lambda_1 \hbar^2$: [angular momentum]² of the solution

c) solution of the angular momentum problem - further separation of variables

$$\begin{aligned} Y(\theta, \phi) &\stackrel{!}{=} \Theta(\theta)\Phi(\phi) \\ \Delta_{\theta\phi} Y(\theta, \phi) &= \Phi(\phi) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \Theta \right] + \frac{\Theta(\theta)}{\sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} \end{aligned}$$

$$\Rightarrow \underbrace{\frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial \Theta}{\partial \theta} \right] + \lambda_1 \sin^2 \theta}_{f(\theta)} = \lambda_2 = \underbrace{-\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2}}_{g(\phi)}$$

$$\begin{aligned} \lambda_2 &= -\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} \\ \Rightarrow \frac{\partial^2 \Phi}{\partial \phi^2} + \lambda_2 \Phi &= 0 \end{aligned}$$

solution $\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm i\sqrt{\lambda_2}\phi}$ ($\sqrt{2\pi}$ - normalization)

boundary condition: $\Phi(\phi) = \Phi(\phi + 2\pi)$

$$\begin{aligned} \Rightarrow \lambda_2 &> 0 \\ \Rightarrow \sqrt{\lambda_2} &= m \quad \text{with } m \text{ being an integer} \\ \Rightarrow \Phi &= \frac{1}{\sqrt{2\pi}} e^{im\phi} \end{aligned}$$

eigenvalue of $\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$:

$$\begin{aligned} \hat{L}_z \psi(r, \theta, \phi) &= \hat{L}_z R(r) \Theta(\theta) \Phi(\phi) \\ &= R(r) \Theta(\theta) \left[-i\hbar \frac{\partial}{\partial \phi} \frac{1}{\sqrt{2\pi}} e^{im\phi} \right] \\ &= m\hbar \psi(r, \theta, \phi) \end{aligned}$$

\Rightarrow angular momentum in z-direction of eigenfunctions:

$$\langle \psi | \hat{L}_z | \psi \rangle = m\hbar \langle \psi | \psi \rangle = m\hbar \quad (\psi \text{ - eigenstate})$$

\Rightarrow only integer multiples of \hbar

the θ -dependence

$$\begin{aligned} \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial \Theta}{\partial \theta} \right] + \lambda_1 \sin^2 \theta &= m^2 \\ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \Theta \right] + \lambda_1 \Theta - \frac{m^2}{\sin^2 \theta} \Theta &= 0 \end{aligned}$$

substitution: $\cos \theta = \zeta \quad -1 \leq \zeta \leq 1$

$$\begin{aligned} \frac{\partial}{\partial \theta} &= \frac{\partial \zeta}{\partial \theta} \frac{\partial}{\partial \zeta} = -\sin \theta \frac{\partial}{\partial \zeta} \\ \frac{1}{\sin \theta} (-\sin \theta) \frac{\partial}{\partial \zeta} \left[\underbrace{\sin \theta [-\sin \theta]}_{\sin^2 \theta = 1 - \cos^2 \theta = 1 - \zeta^2} \frac{\partial}{\partial \zeta} \Theta \right] + \left[\lambda_1 - \frac{m^2}{\sin^2 \theta} \right] \Theta &= 0 \\ \frac{\partial}{\partial \zeta} \left[(1 - \zeta^2) \frac{\partial \Theta}{\partial \zeta} \right] + \underbrace{\left[\lambda_1 - \frac{m^2}{1 - \zeta^2} \right]}_{\text{divergent at } \zeta^2 \pm 1} \Theta &= 0 \end{aligned}$$

divergence at $\zeta = \pm 1$ has to be cancel

expansion around $\zeta \approx +1$

- $\zeta = 1 + x$ with $|x| \ll 1$
- $1 - \zeta^2 = (1 + \zeta)(1 - \zeta) = (2 + x)(-x) = -2x - x^2 \approx -2x$ ($-x^2$ - small)
- $\frac{\partial}{\partial \zeta} = \frac{\partial}{\partial x}$
- $\frac{\partial}{\partial x} [(-2x) \frac{\partial \Theta}{\partial x}] + \left[\lambda_1 - \frac{m^2}{-2x} \right] \Theta = 0$ (λ_1 - can be neglected as $|\lambda_1| \ll \left| \frac{m^2}{x} \right|$)
- $x \frac{\partial}{\partial x} \left[x \frac{\partial \Theta}{\partial x} \right] = \left[\frac{m}{2} \right]^2 \Theta$
- solution $\Theta \approx c x^{\left| \frac{m}{2} \right|}$

\Rightarrow solution behaves like $(1 - \zeta)^{\left| \frac{m}{2} \right|}$ around $\zeta = 1$

analogue

\Rightarrow solution behaves like $(1 + \zeta)^{\left| \frac{m}{2} \right|}$ around $\zeta = -1$

general ansatz

$$\Theta(\zeta) = [1 - \zeta^2]^{\left| \frac{m}{2} \right|} \nu_m(\zeta)$$

resulting differential equation for $\nu_m(\zeta)$

$$(1 - \zeta^2) \frac{d^2 \nu_m}{d\zeta^2} - 2(m+1)\zeta \frac{d\nu_m}{d\zeta} + [\lambda_1 - m(m+1)] \nu_m = 0$$

differentiate equation with equation with respect to ζ

$$(1 - \zeta^2) \frac{d^3 \nu_m}{d\zeta^3} - 2(m+2)\zeta \frac{d^2 \nu_m}{d\zeta^2} + [\lambda_1 - (m+1)(m+2)] \frac{d\nu_m}{d\zeta} = 0$$

same equation as for ν_{m+1} , but for $\frac{d\nu_m}{d\zeta}$

$$\begin{aligned}\Rightarrow \quad \frac{d\nu_m}{d\zeta} &= \nu_{m+1} \\ \Rightarrow \quad \nu_m(\zeta) &= \frac{d^m}{d\zeta^m} \nu_0\end{aligned}$$

now find a solution for ν_0

$$(1 - \zeta^2) \frac{d^2 \nu_0}{d\zeta^2} - 2\zeta \frac{d\nu_0}{d\zeta} + \lambda_1 \nu_0 = 0$$

ansatz for $\nu_0 = \sum_{n=0}^{\infty} a_n \zeta^n$ inserted and put the coefficient in front of ζ^n to zero

$$\begin{aligned}(n+2)(n+1)a_{n+2} - n(n-1)a_n - 2na_n + \lambda_1 a_n &= 0 \\ a_{n+2} &= \frac{n(n+1) - \lambda_1}{(n+2)(n+1)} a_n\end{aligned}$$

again the recursion must break down for a certain $n = L$ to avoid a diverging ν_0

\Rightarrow requirement for $\lambda_1 = L[L+1]$ with L integer solution

$$\Theta(\zeta) = [1 - \zeta^2]^{\frac{m}{2}} \frac{d^m}{d\zeta^m} P_L(\zeta)$$

with $\lambda_1 = L[L+1]$

$$\begin{aligned}\text{and } P_L(\zeta) &= \sum_{n=0}^{L/2} a_{2n} \zeta^{2n} && \text{for even } L \\ &= \sum_{n=0}^{L/2-1} a_{2n+1} \zeta^{2n+1} && \text{for odd } L \\ \text{with } a_{n+2} &= \frac{n(n+1) - L(L+1)}{(n+2)(n+1)} a_n\end{aligned}$$

a_0 and a_1 are chosen such that $\Theta(\zeta)$ is normalized

with proof (but easy to check)

$$P_L(\zeta) = \frac{1}{2^L L!} \frac{d^L}{d\zeta^L} [\zeta^2 - 1]^L$$

$$\begin{aligned}\Theta(\zeta) &= P_L^m : \text{attributed legend polynomial} \\ &= [1 - \zeta^2]^{\frac{|m|}{2}} \frac{d^{L+|m|}}{d\zeta^{L+|m|}} \frac{(\zeta^2 + 1)^L}{2^L L!} (-1)^m \\ &\quad \underbrace{\hspace{1.5cm}}_{\text{cancels}} \quad \underbrace{\hspace{1.5cm}}_{\text{polynomial of degree}} \\ &\quad \text{divergence} \hspace{10cm} L - |m| \\ &\quad \text{at } \zeta = \pm 1\end{aligned}$$

and $\lambda_1 = L[L+1]$ $L = 0, 1, \dots$

and $|m| \leq L$

examples: $P_{L=0}^{m=0} = [1 - \zeta^2]^0 \frac{d^0}{d\zeta^0} \frac{(\zeta^2-1)^0}{2^0 0!} = 1$ (d^0 - no derivative)

similar: $P_1^0 = \zeta$; $P_2^0 = \frac{3}{2}\zeta^2 - \frac{1}{2}$

the whole angular dependence

$$\begin{aligned}\Theta(\theta)\Phi(\phi) &= Y_L^M(\theta, \phi) \\ &= \underbrace{\sqrt{\frac{2L+1}{4\pi} \frac{(L-|m|)!}{(L+|m|)!}}}_{\text{normalization}} P_l^m(\cos\theta) e^{im\phi}\end{aligned}$$

Y_L^m mathematics

- spherical harmonic eigenfunction of $\Delta_{\theta\phi}$
- complete and orthogonal on the surface of the unit sphere

$$\int_0^\pi d\theta \sin\theta \int_{-\pi}^\pi d\phi Y_{L'}^{m'*}(\theta, \phi) Y_L^m(\theta, \phi) = \delta_{LL'} \delta_{mm'}$$

physics

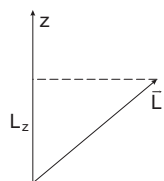
- L =angular momentum quantum number

$$\langle Y_L^M | \hat{L}^2 | Y_L^M \rangle = \hbar^2 L(L+1)$$

- m : $|m| \leq L$

magnetic quantum number

$$\langle Y_L^m | \hat{L}_z | Y_L^m \rangle = \hbar m < \hbar \sqrt{L(L+1)}$$



$$\langle Y_L^m | \hat{L}_z | Y_L^m \rangle^2 < \langle Y_L^m | \hat{L}^2 | Y_L^m \rangle$$

$\Rightarrow \vec{L}$ never points exactly into the z -direction

reason: for $\langle Y_L^m | \hat{L}_z | Y_L^m \rangle^2$ being equal to $\langle Y_L^m | \hat{L}^2 | Y_L^m \rangle$ the other components of \vec{L} would be zero and therefore exactly determined thus contradicting the uncertainty relation.

angular momentum quantum number L	magnetic quantum number m	Y_L^m	name
0	0	1	s
1	+1	$-\frac{1}{\sqrt{2}} \sin \theta e^{i\phi}$	p
	0	$\cos \theta$	
	-1	$\frac{1}{\sqrt{2}} \sin \theta e^{-i\phi}$	
2	+2	$\sqrt{\frac{3}{8}} \sin^2 \theta e^{2i\phi}$	d
	+1	$\sqrt{\frac{3}{8}} \sin \theta \cos \theta e^{i\phi}$	
	0	$\frac{1}{3} [3 \cos^2 \theta - 1]$	
	-1	$-\sqrt{\frac{3}{8}} \sin \theta \cos \theta e^{-i\phi}$	
	-2	$\sqrt{\frac{3}{8}} \sin^2 \theta e^{-2i\phi}$	

5.3 The radial dependence

now $V(r) = -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r}$ Coulomb potential (Z : charge of the core, hydrogen: $Z = 1$)

equation to be solved

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2mE}{\hbar^2} + \frac{2mZe^2}{4\pi\epsilon_0 \hbar^2} \frac{1}{r} - \frac{L[L+1]}{r^2} \right] R = 0$$

A finite angular momentum ($L \neq 0$) gives rise to a repelling potential

The system is determined by two constants: E and $L \Rightarrow m$ has no effect on the energy E

normalization $\hat{=}$ transformation to dimensionless units

$$E = E_R \varepsilon \quad r = a_B \rho \quad E_R: \text{Rydberg energy}$$

a_B : Bohr radius

ε : dimensionless energy

ρ : dimensionless radius

multiply equation with a_B^2

$$\frac{d^2}{d\rho^2} R(\rho) + \frac{2}{\rho} \frac{dR(\rho)}{d\rho} + \left[\frac{2m}{\hbar^2} a_B^2 E_R \varepsilon + \frac{m}{\hbar^2} \frac{Ze^2}{4\pi\epsilon_0} a_B \frac{2}{\rho} - \frac{L(L+1)}{\rho^2} \right] R(\rho) = 0$$

We choose a_B and E_R such that most of the coefficients vanish

$$\begin{aligned}
 \frac{2m}{\hbar^2} a_B^2 E_R &\stackrel{!}{=} 1 & \frac{m}{\hbar^2} \frac{Ze^2}{4\pi\epsilon_0} a_B &\stackrel{!}{=} 1 \\
 &\Downarrow & &\Downarrow \\
 E_R = \frac{\hbar^2}{2ma_B^2} &\Leftarrow a_B = \frac{4\pi\epsilon_0\hbar^2}{me^2Z} \\
 &= \frac{\hbar^2 m^2 e^4 Z^2}{2m[4\pi\epsilon_0]^2 \hbar^4} &= 0.0528 \text{ nm for hydrogen } (Z=1) \\
 E_R &= \frac{me^4 Z^2}{32\pi^2 \epsilon_0^2 \hbar^2} \\
 &= 13,6 \text{ eV} &\text{for hydrogen } (Z=1)
 \end{aligned}$$

\Rightarrow characteristic dimensions (a_B) and energies (E_R) determined without having solved the differential equation

differential equation to be solved:

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left[\varepsilon + \frac{2}{\rho} - \frac{L(L+1)}{\rho^2} \right] R(\rho) = 0$$

now: solution similar as for the harmonic oscillator

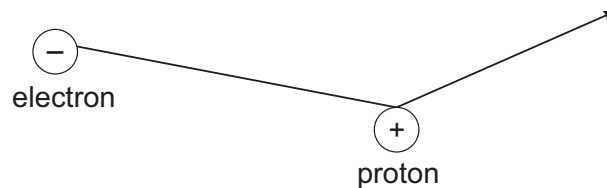
- asymptotic case ($\rho \rightarrow +\infty$)

$$\frac{d^2 R}{d\rho^2} + \varepsilon R = 0$$

- a) $\varepsilon > 0 \Rightarrow$ oscillating solution $R \sim e^{\pm i\sqrt{\varepsilon}\rho}$

\Rightarrow free particle

– so-called scattering states



– possible for all energies $\varepsilon > 0$

– not considered further

- b) $\varepsilon < 0 \Rightarrow$ exponentially localized solution

$$R \sim e^{-\sqrt{-\varepsilon}\rho}$$

– bound state

– further investigated

- ansatz

$$R(\rho) = e^{-\sqrt{-\varepsilon}\rho} \sum_{n=0}^{\infty} a_n \rho^n$$

- insert the ansatz into the differential equation and compare the coefficients in front of ρ^n

\Rightarrow recursion formula for a_n

\Rightarrow recursion must terminate to avoid divergence

\Rightarrow condition for ε

- termination at n with $a_{n+1} = 0$

$$\varepsilon = -\frac{1}{n^2}$$

real energy

$$E = -E_R \frac{1}{n^2}$$

radius dependence

$$R(\rho) = e^{-\sqrt{-\varepsilon}\rho} L_{n+1}^{2L+1}(\rho) \rho^L$$

with the attributed Laguerre polynomial

$$L_{n+1}^{2L+1}(\rho) = \underbrace{\frac{d^{2L+1}}{d\rho^{2L+1}} \left[e^\rho \frac{d^{n+L}}{d\rho^{n+L}} (\rho^{n+L} e^{-\rho}) \right]}_{\text{polynomial of order } n_r = n - L - 1 \text{ with } n_r \text{ zeros}}$$

polynomial of order $n_r = n - L - 1$ with n_r zeros

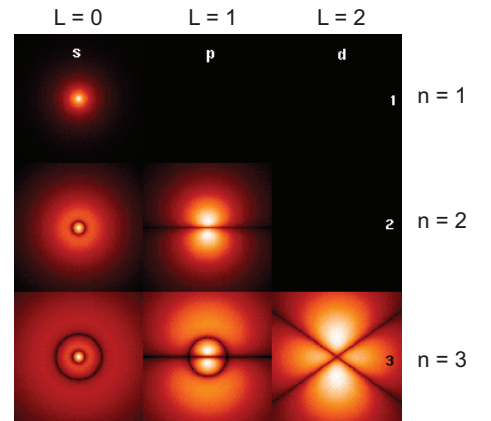
complete wave function

$$\psi_{nLm}(r, \theta, \phi) = Y_L^m(\theta, \phi) R\left(\frac{r}{a_B}\right)$$

with the energy $E = -E_R \frac{1}{n^2}$

and $|m| \leq L$ and $L \leq n - 1$

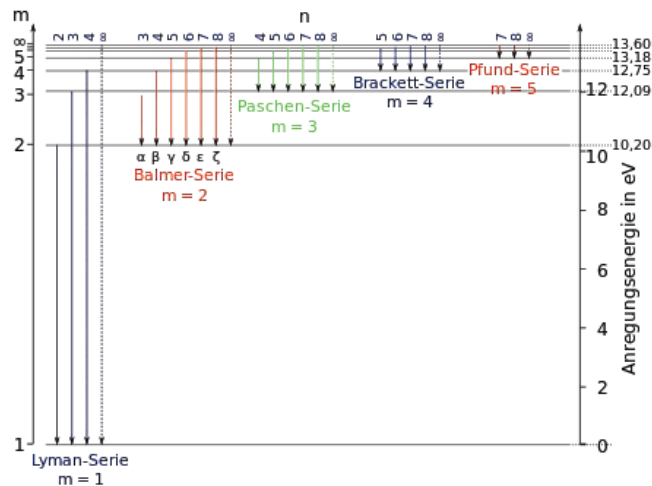
n	L	m	function	energy E	number of zeros radial direction $n_r = n - L - 1$
1	0	0	$\frac{1}{\sqrt{\pi a_B^3}} e^{-\frac{r}{a_B}}$	$-E_R$	0
2	0	0	$\frac{1 - \frac{r}{a_B}}{\sqrt{8\pi a_B^3}} e^{-\frac{r}{2a_B}}$	$-\frac{E_R}{4}$	1
	1	0	$\frac{\cos \theta r}{\sqrt{128\pi a_B^5}} e^{-\frac{r}{2a_B}}$	$-\frac{E_R}{4}$	0
		± 1	$\frac{\sin \theta r}{\sqrt{512\pi a_B^5}} e^{-\frac{r}{2a_B}}$	$-\frac{E_R}{4}$	0



5.4 Optical response of hydrogen

emission of photons – level transitions

- $\hbar\omega = E_n - E_m = -E_e \left[\frac{1}{n^2} - \frac{1}{m^2} \right]$



picture Balmer serie

remarks

- spectral positions of emission lines very well reproduced (error $< 10^{-2}$)

but

- small deviations + line splitting \Rightarrow degeneracy lifted
- transition rates between different states vary by many orders of magnitude

degeneracy of a state n

- energy $\hat{H} \Rightarrow n \Rightarrow E_n = -E_R \frac{1}{n^2}$
- angular momentum \hat{L}^2 : $L = 0 \dots n-1 \Rightarrow n$ times degenerate
- z -component \hat{L}_z

$$\underbrace{m = -L \dots + L}_{2L+1 \text{ states}} \Rightarrow \sum_{L=0}^{n-1} [2L+1] = n^2 \text{ times degenerate}$$

- spin \hat{s}

$$\underbrace{m_s = \pm \frac{1}{2}}_{2 \text{ states}} \Rightarrow 2n^2 \text{ degenerate}$$

To each energy level n of the hydrogen atom belong $2n^2$ states.

5.5 The Spin

5.5.1 Magnetic moments

- z -component of angular momentum: $\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$
- ϕ -dependent part of an eigenstate $\psi_m \sim e^{im\phi}$
 $\Rightarrow \hat{L}_z |\psi_m\rangle = \hbar m |\psi_m\rangle$ m must be an integer!
- relation between angular momentum and magnetic moments (classical approach)
magnetic dipole moment: $\vec{M} = \frac{1}{2} \sum_i \vec{r}_i \times (q_i \vec{v}_i)$

for equal charges and masses

$$\vec{M} = \frac{q}{2m} \sum_i \vec{r}_i \times \vec{p}_i = \frac{q}{2m_e} \vec{L}$$

magnetic moment \sim angular momentum

\Rightarrow states with non-vanishing angular momentum should show a magnetic response

quantum mechanical expectation: Particles in eigenstates of the angular momentum should have quantized magnetic momenta

$$\hat{M} |\psi_m\rangle = \mu_B \cdot m |\psi_m\rangle$$

with Bohr's magneton $\mu_B = \frac{\hbar q}{2m_e}$

from classical electrodynamics:

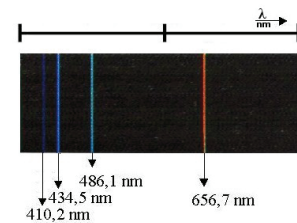
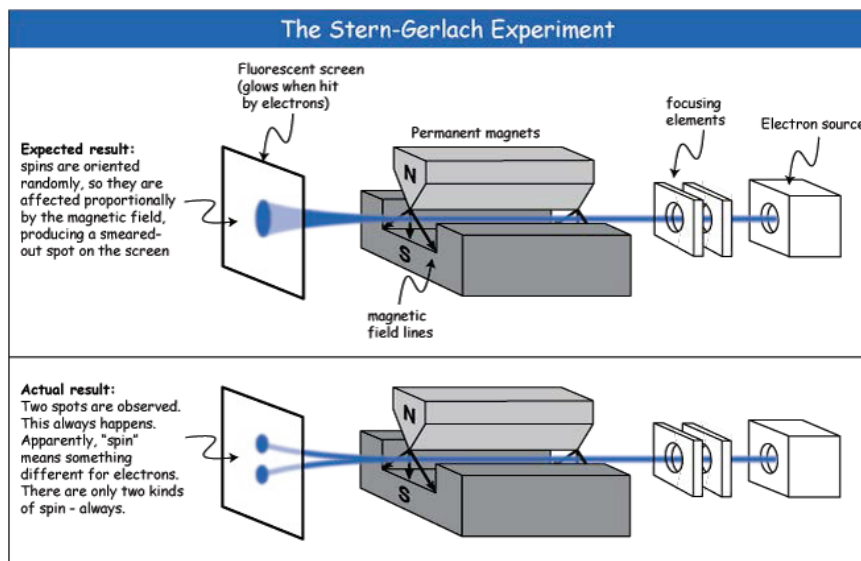
interaction energy: $W = -\vec{M} \cdot \vec{B}(\vec{r})$ \vec{B} : magnetic induction

force on a magnetic dipole $\hat{F} = -\nabla W = \nabla [\vec{M} \cdot \vec{B}(\vec{r})]$

5.5.2 The Stern-Gerlach-Experiment

aim: measure the angular momentum / magnetic moment of electrons

method: deflection in an inhomogeneous magnetic field

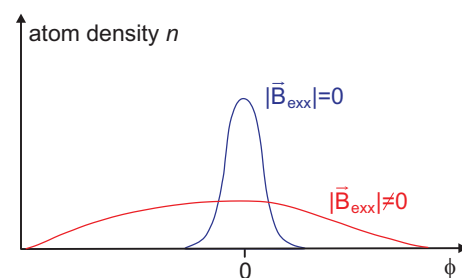


instead of electrons:

- atoms with one shell electron (Na, K, Ag, ...)
- no charge effects as this would be the case for free electrons
- easy to be detected
- cations (Ag^+ , Na^+ , K^+ ...) have (almost) no magnetic moment \rightarrow magnetic response of the neutral atom must be due to the shell electron

classical expectation:

- If the electron has a magnetic moment the beam should spread in the presence of a magnetic field.
- reason: classical magnetic momenta are not discretized

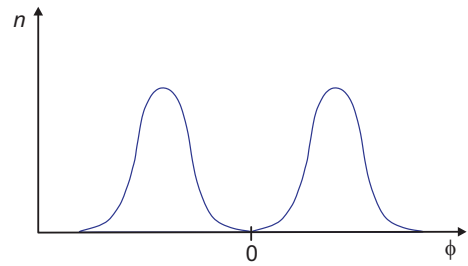


expectation from simple quantum mechanical considerations

- only angular momentum in \vec{B} -field direction counts $\sim L_z$
- as $-L \leq m \leq L \Rightarrow$ splitting into an odd number of beams expected

experimental observation

- splitting into two beams
 \Rightarrow angular momentum of single electron
 measured $m_s = \pm \frac{1}{2}$



\hat{s}_z : operator of the z -component of the angular momentum of a single electron (similar to \hat{L}_z)

\hat{s}^2 : operator of the total angular momentum of a single electron (similar to \hat{L}^2)

$|\psi\rangle$: eigenstate of \hat{s}_z , and \hat{s}^2 and \hat{H}

$\hat{s}_z|\psi\rangle = m_s\hbar|\psi\rangle$ with $m_s = \pm \frac{1}{2}$

residual relations still hold:

$$-L_s \leq m_s \leq L_s \Rightarrow L_s = \frac{1}{2}$$

$$\hat{s}^2|\psi\rangle = \hbar^2 L_s(L_s + 1)|\psi\rangle = \frac{3}{4}\hbar^2|\psi\rangle$$

but

no wave function like $\sim e^{im_s\phi}$ can be attributed to $|\psi\rangle$

It can be derived, that $-L_s \leq m_s \leq L_s$ must always hold, that m_s can only vary in integer steps and that L can have either integer or half integer values.

magnetic response of single electrons

expected: $M_z = -m_s\mu_B$ with $m_s = \pm \frac{1}{2}$

observed: $M_z = -g_e m_s \mu_B$ with the gyromagnetic factor $g = 2.0023193$ (2.0 – interaction with virtual positron, 0.0023193 – interaction with other vacuum particles)

for comparison: gyromagnetic ratio of:

the proton +5,585

the neutron -3.826

$|g| \neq 1$ is a hint to a nontrivial internal structure or to an interaction with other fields

5.5.3 Normal Zeeman effect

response of atoms to strong magnetic fields

modified Hamiltonian

$$\begin{aligned}
 \hat{H} &= \hat{H}_0 + \hat{H}_w & \hat{H}_0 : & \text{Hamiltonian of hydrogen with known eigenstates} \\
 \hat{H} &= -\vec{B}_{\text{ext}} \vec{\hat{M}} & & \text{for simplicity } \vec{B}_{\text{ext}} = B \vec{e}_z \text{ with } B = \text{const.} \\
 \Rightarrow \hat{H}_w &= -B \hat{M}_z & \hat{M}_z : & \text{magnetic moment in } z\text{-direction} \\
 & & \hat{M} &= -\frac{\mu_B}{\hbar} [\hat{L}_z + g \hat{S}_z] \\
 \hat{H}_w &= \frac{\mu_B}{\hbar} B [\hat{L}_z + g \hat{S}_z]
 \end{aligned}$$

as \hat{H}_0 does neither depend on \hat{L}_z nor on \hat{S}_z : $[\hat{H}_0, \hat{H}_w] = 0$

$\Rightarrow \hat{H}_0$ and \hat{H}_w have a joint eigenfunction system with new eigenvalues

$$\begin{aligned}
 E|n, L, m, m_s\rangle &= (\hat{H}_0 + \hat{H}_w)|n, L, m, m_s\rangle \\
 E|n, L, m, m_s\rangle &= E_n|n, L, m, m_s\rangle + \frac{\mu_B}{\hbar} [\hat{L}_z + g \hat{S}_z] |n, L, m, m_s\rangle \\
 &= \left[E_n + \frac{\mu_B B}{\hbar} [\hbar m + g \hbar m_s] \right] |n, L, m, m_s\rangle
 \end{aligned}$$

new energies shifted by $\Delta E = \mu_B [m + g m_s] B \Rightarrow$ splitting of the m -degeneracy

but

- only true, if internal magnetic fields caused by spin-orbit coupling are smaller than B (otherwise: anomalous Zeeman effect)

The normal Zeeman effect is a

- lucky case, because $[\hat{H}_0, \hat{H}_w] = 0$

Usually this is not the case: $[\hat{H}_0, \hat{H}_w] \neq 0$

\Rightarrow no joint eigenfunction system

\Rightarrow perturbation theory required

5.6 Perturbation theory for hydrogen

5.6.1 General perturbation theory

problem: perturbed system $\hat{H} = \hat{H}_0 + \hat{H}_w$

known: eigenstates of \hat{H}_0 with $E_0 = \hat{H}_0 |\psi_0\rangle$

looking for E and $|\psi\rangle$ with $\hat{H}|\psi\rangle = E|\psi\rangle$

approximate solution

- assuming \hat{H}_w to be small / to have little effect

\Rightarrow small corrections to $|\psi\rangle$ and E_0

- introduction of a "smallness" parameter ε

\Rightarrow used to order terms according to their importance

\Rightarrow will be finally set to 1

$$\hat{H} = \hat{H}_0 + \varepsilon \hat{H}_w$$

a) $|\psi_0\rangle$ is non degenerate

$$|\psi\rangle = \sum_{n=0}^{\infty} \varepsilon^n |\psi_n\rangle \quad \text{system of } |\psi_n\rangle : \text{ complete and orthogonal}$$

in particular: $\langle \psi_0 | \psi_1 \rangle = 0$ must hold

$$E = \sum_{n=0}^{\infty} \varepsilon^n E_n$$

insert into the eigenvalue equation

term of order ε^0 : $\hat{H}_0|\psi_0\rangle = E_0|\psi_0\rangle \Rightarrow$ unperturbed system

term of order ε^1

$$\begin{aligned} \hat{H}_0|\psi_1\rangle + \hat{H}_w|\psi_0\rangle &= E_0|\psi_1\rangle + E_1|\psi_0\rangle \quad |\langle \psi_0| \\ \langle \psi_0|\hat{H}_0|\psi_1\rangle + \langle \psi_0|\hat{H}_w|\psi_0\rangle &= E_0\langle \psi_0|\psi_1\rangle + E_1\langle \psi_0|\psi_0\rangle \\ \underbrace{E_0\langle \psi_0|\psi_1\rangle}_0 &\quad \underbrace{0}_0 \quad \underbrace{1}_1 \end{aligned}$$

first energy correction: $E_1 = \langle \psi_0 | \hat{H}_w | \psi_0 \rangle$

b) degenerate case: $\hat{H}_0|\psi_0^m\rangle = E_0|\psi_0^m\rangle$ ($m = 1 \dots M$)

\Rightarrow initial state $|\psi_0\rangle$ can be a linear combination of $|\psi_0^m\rangle$

$$|\psi_0\rangle = \sum_{m=1}^M a_m |\psi_0^m\rangle$$

still the same expansion is performed $|\psi\rangle = \sum_{n=0}^{\infty} \varepsilon^n |\psi_n\rangle$ and $\langle \psi_1 | \psi_0^m \rangle = 0$ for all m

term of order ε^1

$$\hat{H}_0|\psi_1\rangle + \hat{H}_w \sum_m^M = 1 a_m |\psi_0^m\rangle = E_0|\psi_1\rangle + E_1 \sum_{m=1}^M a_m |\psi_0^m\rangle \quad |\langle \psi_0^{m'}|$$

for each $m' = 1 \dots M$

$$\sum_{m=1}^M a_m \langle \psi_0^{m'} | \hat{H}_w | \psi_0^m \rangle = E_1 \sum_{m=1}^M a_m \underbrace{\langle \psi_0^{m'} | \psi_0^m \rangle}_{\delta_{mm'}} = E_1 a_{m'}$$

eigenvalue problem

$$\hat{H}'_w \vec{a} = E_1 \vec{a}$$

with $\vec{a} = (a_1, a_2 \dots a_M)^T$

$$\hat{H}'_{w_{m'm}} = \langle \psi_0^{m'} | \hat{H}_w | \psi_0^m \rangle$$

\Rightarrow projection of \hat{H}_w into the subspace spanned by the $|\psi_0^m\rangle$

In general \hat{H}'_w must be diagonalized numerically but often a clever choice of basic functions allows to diagonalize \hat{H}'_w . The different eigenvalues resulting from the diagonalization of \hat{H}'_w are the first order corrections to the energy. Usually the M -times degeneracy of the unperturbed eigenstate is lifted and M different eigenvalues appear.

5.6.2 Spin-orbit-coupling

- electron on its orbit
 - spin of the electron
- } produce magnetic moments
} \Rightarrow interaction

$$\hat{H}_w = \frac{\mu_0 e^2}{8\pi m_e^2} \frac{\hat{S} \hat{L}}{\hat{r}^3} \quad \hat{S} : \text{spin}$$

- looking for good eigenfunctions or relevant quantum numbers

$$\bullet \quad \underbrace{\left[\hat{S} \hat{L}, \hat{L}^2 \right]}_0 = \hat{S} \underbrace{\left[\hat{L}, \hat{L}^2 \right]}_0 + \underbrace{\left[\hat{S}, \hat{L}^2 \right]}_0 \hat{L} = 0$$

\Rightarrow total orbital angular momentum not affected (conserved)

$\Rightarrow L$ remains a good quantum number

but $\left[\hat{S} \hat{L}, \hat{L}_z \right] \neq 0$ because $\left[\hat{L}_{x/y}, \hat{L}_z \right] \neq 0$

$\Rightarrow m$ is not a good quantum number

- express $\hat{S} \hat{L}$ by conserved quantities

$$\hat{S} \hat{L} = \frac{1}{2} \left[(\hat{S} + \hat{L})^2 - \hat{L}^2 - \hat{S}^2 \right]$$

$(\hat{\vec{S}} + \hat{\vec{L}} - [\text{total angular momentum}]^2 \Rightarrow \text{conserved}; \hat{\vec{L}}^2 - [\text{total orbital angular momentum}]^2 \Rightarrow \text{conserved}; \hat{\vec{S}}^2 - [\text{total spin angular momentum}]^2 \Rightarrow \text{conserved})$

- new good quantum numbers: j and m_j
with $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$ operator of total angular momentum

$$\begin{aligned}\hat{\vec{J}}^2 |n, L, j, m_j\rangle &= \hbar^2 j(j+1) |n, L, j, m_j\rangle \\ \text{and } \hat{J}_z |n, L, j, m_j\rangle &= \hbar m_j |n, L, j, m_j\rangle \\ j &= L \pm \frac{1}{2} \quad (j - \text{total}, L - \text{orbit}, \frac{1}{2} - \text{spin})\end{aligned}$$

$-j \leq m_j \leq j$: z -component of the total angular momentum

- energy shift

$$\begin{aligned}\Delta E &= \langle n, L, j, m_j | \hat{H}_w | n, L, j, m_j \rangle \\ &= \frac{\mu_0 e^2}{8\pi m_e^2} \langle n, L, j, m_j | \frac{\hat{\vec{S}} \hat{\vec{L}}}{r^3} | n, L, j, m_j \rangle \\ &= \frac{\mu_0 e^2}{8\pi m_e^2} \int_0^\infty dr 4\pi r^3 R_{nL}^*(r) \frac{1}{r^3} R_{nL}(r) \\ &\quad \times \frac{\hbar^2}{2} \left[j(j+1) - L(L+1) - \frac{3}{4} \right] \\ &= \bar{a} \frac{1}{2} \left[j(j+1) - L(L+1) - \frac{3}{4} \right]\end{aligned}$$

$(R_{nL}^*, R_{nL} - \text{radial dependent part of hydrogen eigenfunctions})$

with

$$\bar{a} = \frac{E_R}{n^3} \frac{\alpha^2}{L \left[L + \frac{1}{2} \right] [L + 1]}$$

with the fine structure constant

$$\alpha = \frac{1}{4\pi\epsilon_0 c} \frac{e^2}{\hbar} \approx \frac{1}{137}$$

\Rightarrow energy shift due to spin-orbit coupling $\approx 10^{-4} \dots 10^{-5} E_R$

new

\Rightarrow states $\hat{=}$ so-called fine structure

5.6.3 Other perturbations

a) relativistic corrections

reason: correct kinetic energy:

$$E = \sqrt{m_0^2 c^4 + p^2 c^2} - m_0^2 c^2$$

$$\approx m_0 c^2 + \frac{p^2}{2m_0} - \underbrace{\frac{1}{8} \frac{p^4}{m_0^3 c^2}}_{\hat{H}_w} - m_0^2 c^2$$

\hat{H}_w : important for heavy atoms and electron orbits close to the core

effect: energy splitting of L -terms of the order of α^2

\hat{H}_w comparable with spin-orbit-splitting ($\approx 10^{-3}$ eV

spin is also a relativistic effect!

b) Hyperfine structure $\hat{=}$ coupling to the magnetic field of the core

$$\hat{H}_w \sim \hat{\vec{J}} \hat{\vec{I}}$$

$\hat{\vec{J}}$ - total angular momentum of the electrons

$\hat{\vec{I}}$ - total angular momentum of the core

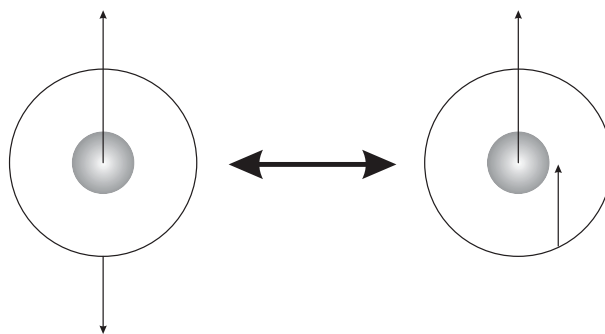
treatment: very similar to spin-orbit-coupling

but much weaker $\lesssim 10^{-5}$ eV

still important because

- measure of the properties of the nucleus
- microwave transitions in astronomy

example: hydrogen



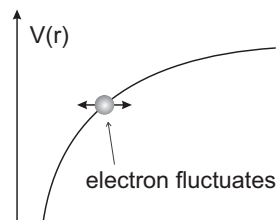
\Rightarrow emission of radiation with $\lambda = 21$ cm

⇒ measure of hydrogen concentration in the universe

- high precision clocks are locked to a hyperfine transition in the microwave domain (e.g. caesium)

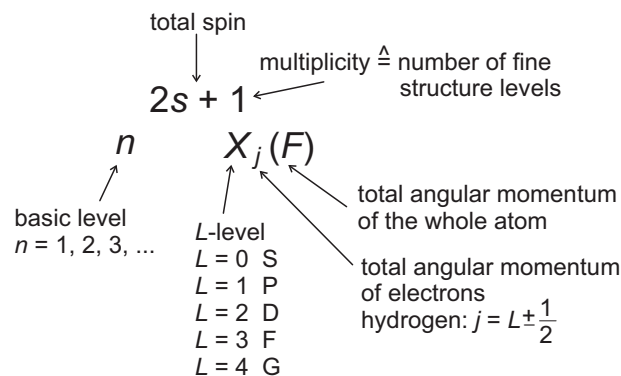
c) Lamb-Shift

- coupling to virtual photons
- permanent emission and absorption of virtual photons causes a fluctuation in the asymmetric potential



⇒ level dependent energy shift slightly bigger than Hyperfine structure splitting

5.6.4 Index scheme of atomic levels



also used for many-electron-systems

5.7 Selection rules for optical transitions

5.7.1 Dipole element

source of radiation: polarization

classical: $\vec{P} = -Ne\vec{r}$ (N – density of atoms, e – charge, \vec{r} – elongation)

quantum mechanical:

- evolution of general state

$|\Psi\rangle = \sum_n c_n(t)|\psi_n\rangle$ (c_n – evolving amplitude, unperturbed $c_n(t) = ce^{-i\frac{E_n}{\hbar}t}$, $|\psi_n\rangle$ – eigen-

state)

- polarization without perturbation

$$\begin{aligned}\langle \vec{P}(t) \rangle &= -eN \langle \Psi(t) | \hat{\vec{r}} | \Psi(t) \rangle \\ &= -eN \sum_a \sum_b c_a^* c_b \langle \psi_a | \hat{\vec{r}} | \psi_b \rangle\end{aligned}$$

term $a = b$

$$\vec{P}_{aa} = -eN |c_a|^2 \langle \psi_a | \hat{\vec{r}} | \psi_a \rangle = -eN |c_a|^2 \int d^3r |\psi_a(\vec{r})|^2 \vec{r}$$

($|c_a|^2$ - no evolution in the unperturbed case, $\int d^3r |\psi_a(\vec{r})|^2 \vec{r}$ - static dipole moment = 0 for hydrogen)

- optical transitions: terms $a \neq b$

$$\vec{P}_{ab} = -eN c_a^* c_b \langle \psi_a | \hat{\vec{r}} | \psi_b \rangle$$

unperturbed case: $\vec{P}_{ab}(t) \sim e^{-i \frac{E_b - E_a}{\hbar} t}$

\Rightarrow can excite radiation with frequency $\omega = \frac{E_b - E_a}{\hbar}$

spontaneous transition rate between states $|\psi_a\rangle, |\psi_b\rangle$

$$\sim |\langle \psi_a | \hat{\vec{r}} | \psi_b \rangle|^2 \quad \vec{r} \text{ dipole element} \sim \text{polarization}$$

5.7.2 Selection rules for spin

weak spin-orbit coupling (not true for heavy elements): $|\psi_a\rangle \approx |X_a\rangle |\vec{S}_a\rangle$ ($|X_a\rangle$ - space dependent part, $|\vec{S}_a\rangle$ - spin dependent part)

$$\begin{aligned}\langle \psi_a | \hat{\vec{r}} | \psi_b \rangle &= \langle \vec{S}_a | \langle X_a | \hat{\vec{r}} | X_b \rangle | \vec{S}_b \rangle \\ &= \langle \vec{S}_a | \vec{S}_b \rangle \langle X_a | \hat{\vec{r}} | X_b \rangle\end{aligned}$$

$\underbrace{\hspace{1.5cm}}$

1 for identical spins

0 for opposite spins

\Rightarrow spin remains conserved in an optical transition

5.7.3 Magnetic quantum number m

a) looking for fields polarized in z -direction

$\Rightarrow P_z$ matters

$\Rightarrow \langle \psi_a | z e_z | \psi_b \rangle$

$$= \int_0^\infty dr r^2 R_a^*(r) R_b(r) r \int_0^\pi d\theta \sin \theta \Theta_a^*(\theta) \Theta_b(\theta) \cos \theta \underbrace{\int_{-\pi}^\pi d\phi e^{-im_a \phi} e^{im_b \phi}}_{\delta_{m_a m_b}}$$

$\Rightarrow m_a = m_b$

b) field polarized in x -direction $x = r \sin \theta \cos \phi$

$$\langle \psi_a | x \vec{e}_x | \psi_b \rangle = \int_0^\infty dr r^2 R_a^*(r) R_b(r) r \int_0^\pi d\theta \sin^2 \theta \Theta_a^* \Theta_b \underbrace{\int_{-\pi}^\pi d\phi e^{i(m_b - m_a)\phi} \frac{1}{2} [e^{i\phi} + e^{-i\phi}]}_{\frac{1}{2} [\delta_{m_b+1, m_a} + \delta_{m_b-1, m_a}]}$$

$\Rightarrow m_a = m_b \pm 1$

without proof: left/right circular $\Rightarrow \Delta m = +1 / \Delta m = -1$

5.7.4 General transition rules

- up to now: only ϕ -integration discussed
- θ -integration: more cumbersome
 - result: $\Delta L = \pm 1$
 - mathematical background $\langle \psi_a | \vec{r} | \psi_b \rangle \neq 0$
only, if $\int d^3r \psi_a^*(\vec{r}) \psi_b(\vec{r}) \vec{r}$ (\vec{r} - odd)
the integrand is even

$\Rightarrow \psi_a^*(\vec{r})\psi_b(\vec{r})$ must be odd

$$\psi_a^*(-\vec{r})\psi_b(-\vec{r}) = -\psi_a^*(\vec{r})\psi_b(\vec{r})$$

\Rightarrow parity must change

– physical background: spin 1 of the photon is absorbed by orbital angular momentum

summary optical transitions:

$\Delta m_s = 0 \quad \Rightarrow \quad$ no spin flip

$\Delta m = 0, \pm 1$

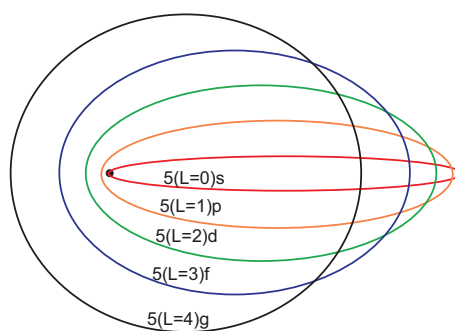
$\Delta L = \pm 1 \quad \Rightarrow \quad$ parity change

5.8 Rydberg atoms

Rydberg atoms = atoms with one electron in a highly excited states (n up to 500)

highly excited electron:

- "sees" just a core with a single positive charge \Rightarrow hydrogen like behavior for all atoms (in experiments: usually *Rb*-atoms)
- behaves very much like a "classical" particle on an orbit
 - \Rightarrow Bohr-Sommerfeld-model works
 - \Rightarrow Like planetary orbits



- circular orbit: $L = n - 1$ in the $x - y$ -plane for $m = \pm L$
- elliptic orbit: $L < n - 1$ the smaller L the higher the ellipticity

states with circular orbit $L = n - 1, m = L$

- balance of forces: centripetal force = Coulomb force

$$\frac{m_e v^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2} \quad r : \text{radius of orbit}$$

- angular momentum

$$L_z = \hbar m = \hbar(n-1) = m_e v \cdot r \Rightarrow v = \frac{\hbar(n-1)}{m_e r}$$

- combination of both equations

$$\begin{aligned} r &= \frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e} (n-1)^2 \\ &= a_B (n-1)^2 = (n-1)^2 \cdot 52,9 \cdot 10^{-12} \text{ m} \end{aligned}$$

usual hydrogen atom ($n = 1$) $r \approx 0.053 \text{ nm}$

Rydberg atom ($n = 100$) $r \approx 0.5 \text{ } \mu\text{m}$ (Here the simple formula for does not apply!)

\Rightarrow almost macroscopic

creation of Rydberg atoms

- a) energy exchange with fast electron beams (inelastic scattering) \Rightarrow creation of states with large L
- b) charge exchange excitation between ions and neutral atoms
 $A^+ + B \rightarrow A^* + B^+ \Rightarrow$ creation of states with large L
- c) optical excitation \Rightarrow creation of states with lower L

Life time of Rydberg atoms for low densities

- usually extremely long (up to s) compared with excitations of low n (e.g. $n = 2 : ns$)
- explanation for $L = n - 1$

– decay can only happen via optical transitions

$$\Rightarrow \Delta L = \pm 1$$

$$\Rightarrow \Delta n = 1 \text{ decay in very small steps}$$

$$- \hbar\omega = E_R \left[\frac{1}{(n-1)^2} - \frac{1}{n^2} \right] \approx 2 \frac{E_R}{n^3}$$

\Rightarrow usually in the microwave domain

- life time limited by optical decay $\sim \frac{1}{\omega^3}$
 $\Rightarrow \tau \sim n^9$
- Only true for optical decay: Collisions reduce the life time!

properties of Rydberg atoms

- extremely large
- very sensitive to electric fields:
 - electron weakly bound \Rightarrow easy to be shifted
 - strong polarizability
- very sensitive to magnetic fields
 - electron forms a huge ring current
 - strong magnetic polarizability
- very sensitive to microwave photons
 - Rydberg atom senses single photons in a microwave cavity
 Nobel prize physics 2012 Serge Haroche
- strong mutual interaction between different Rydberg atoms

The transition frequency of a Rydberg atom depends on the excitation state of its neighbors

\Rightarrow strong collective effects

\Rightarrow The excitation of a single atom can prevent the optical excitation of its neighbors (Rydberg blockade).

\Rightarrow basis of single photon processing

applications of Rydberg atoms

- important in interstellar gases (first observations of respective spectral lines)
- important in plasmas
- potential basis of photon based quantum computing

6 Higher order atoms

6.1 General rules

- general structure of hydrogen levels preserved
- shape of electron wave functions, in particular of the angular dependence preserved

but

- degeneracy of n -level lifted
 - the higher the angular momentum L the higher the energy
 - higher L -levels of a certain n may overlap with low L -levels of $n + 1$ -states
 - different electrons interact
- ⇒ Complicated many particle effects make a quantitative determination of energy levels of higher elements difficult or even impossible

many particle effects

- electrons: fermions

Electron systems have antisymmetric wave functions with respect to an exchange of electrons

e.g. for 2 electrons a and b

$$|\psi\rangle = |a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2$$

$|\psi\rangle$ – total wave function, a – electron, $| \rangle_1$ – state 1, $|b\rangle_1$ – electron b in state 1, $|a\rangle_2$ – electron a in state 2

exchange of electrons a and b

$$|\psi\rangle' = |b\rangle_1|a\rangle_2 - |a\rangle_1|b\rangle_2 = -|\psi\rangle$$

In case of equal states 1 and 2:

$$|\psi\rangle = |a\rangle_1|b\rangle_1 - |b\rangle_1|a\rangle_1 = 0$$

⇒ two electrons cannot occupy the same state (Pauli's principle)

⇒ electrons "fill" all available states beginning with those having the lowest energy

- Strictly speaking individual electrons cannot be attributed to a certain energy level. One electron simultaneously occupies many levels.
 \Rightarrow exchange interaction
 \Rightarrow effective reduction of repelling forces between different electrons
- Within one L -level states with parallel spins are preferred.
- Electrons tend to form spherically symmetric charge distributions
 \Rightarrow Electrons fill all m -levels before starting to occupy the next L -level
- oxidation states of an element: number of electrons to be lost (positive) or gained (negative) to attain a more stable configuration (often a complete shell)

6.2 Periodic system of elements

- elements ordered according to their chemical properties $\hat{=}$ according to the wave function of the outer electron
- different rows/periods: quantum numbers n of the outer electron
- different columns/groups: quantum numbers L of the outer electron

simplified notation: $H : 1s^1$ ($1n, s - L, ^1 -$ number of electrons)

1. period $n = 1$ K -shell

${}_1H : 1s^1 \quad L = 0$

${}_2He : 1s^2 \quad L = 0 \quad 2 \text{ electrons with different spins}$

2. period $n = 2$ L -shell

${}_3Li : [He]2s^1 \quad L = 0 \quad 1 \quad \text{outer electron} = \text{oxidation states} \quad +1$

${}_4Be : [He]2s^2 \quad L = 0 \quad 2 \quad +2$

${}_5B : [He]2s^2 2p^1 \quad 2+1 \quad +3$

${}_6C : [He]2s^2 2p^2 \quad 2+2 \quad +2, +4, -4$

\vdots

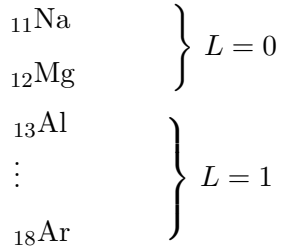
(from ${}_5B$ until ${}_{10}Ne$: $L = 1$)

He, Ne: closed shells

- spherical symmetric electron configuration

\Rightarrow very stable

3. period $n = 3$ M -shell



$3d^x (L = 2)$ energetically higher than $4s^x (L = 0)$

$\Rightarrow 4s$ occupied first

4. period $n = 4$ N -shell

${}_{19}\text{K} : [\text{Ar}]4s^1 \Rightarrow$ oxidation states $+1$

${}_{20}\text{K} : [\text{Ar}]4s^2 \Rightarrow$ oxidation states $+2$

continued with 3. period M -shell

${}_{21}\text{Sc} : [\text{Ar}]3d^1 4s^2$

\vdots

${}_{29}\text{Zn} : [\text{Ar}]3d^{10} 4s^1$ (d^{10} – prefers to fill $3d$ first)

${}_{30}\text{Zn} : [\text{Ar}]3d^{10} 4s^2$

transition metals $[\text{Sc} \rightarrow \text{Zn}]$

- d -shell rather inactive
- chemical properties mainly determined by $4s^2$ electrons
- similar properties
- weakly bound outer electrons \Rightarrow metals
- oxidation states: mainly $+2$ (except Sc with $+3$)

4. period $n = 4$ N -shell

${}_{31}\text{Ga} : [\text{Ar}]3d^{10} 4s^2 4p^1$ oxidation number $+3$ ($[\text{Ar}]3d^{10}$ – closed shells, $4s^2 4p^1$ – weakly bound)

\vdots

${}_{36}\text{Kr} : [\text{Ar}]3d^{10} 4s^2 4p^6$

Kr: closed shells \Rightarrow noble gas

$4s^2$ weakly bound \Rightarrow oxidation state $+2$ possible

process of breaking the conventional order repeats several times

⇒ several groups of transition metals

$(n-1)d^{1-10}ns^2$ $n = 4, 5, 6, 7$ ($1-10$ – filled in the group)

⇒ rare earth metals

Lanthanides $[\text{Xe}]4f^{0-14}5d^16s^2$ ($5d^16s^2$ – weakly bound)

metals with main oxidation number +3

Actinide $[\text{Rn}]5f^x6d^17s^2$ $x = 0...14$

sometimes $[\text{Rn}]5f^{x'}7s^2$

also

2–3 weakly bound electrons

oxidation number: +2 or +3

ionization energies within one period

- 1st group (e.g. $_{11}\text{Na}$)

1 electron orbits the closed shell of $_{10}\text{Ne}$ and "sees" one positive charge \approx hydrogen problem (e.g. $3s$)

⇒ ionization energy $\approx \frac{E_R}{n^2}$

- 8th group (e.g. $_{18}\text{Ar}$)

8 electrons orbit the closed shell of $_{10}\text{Ne}$, mainly on different m -orbits

⇒ weak mutual interaction between the outer electrons

⇒ Each of the 8 electrons "sees" an approximately eight times positively charged core

- as $E_R \sim Z^2$ (Z - charge of the core) and $a_B \sim \frac{1}{Z}$: high ionization energy and small atomic radius

within one period (from the 1st to the 8th group):

- the ionization energy increases
- the diameter of the atom decreases

for growing periods n

- outer electrons become weaker bound (higher n -states)

- ionization energy decreases
- diameter increases

nature of the resulting material

- weakly bound outer electron / small ionization energy: metals
 - 1st, 2nd (alkali metals)
 - more pronounced for heavier elements
 - all transition elements
 - ⇒ metallic bonding: electrons float between positively charged ions
- stronger bound electrons (upper right of periodic table): nonmetals
 - try to complete their shell
 - establish molecular bonds
 - nonmetals: semiconductors (solids), diatomic molecules (gases and liquids)
- completed shells = noble gases
 - single atom gases

7 Molecules

7.1 Born-Oppenheimer-Approximation

molecules = composed of many atoms

⇒ complicated many body problem including electrons and cores

hierarchy of interactions

a) electronic interaction

- cores: assumed to be fixed.
- only Coulomb interaction between electrons

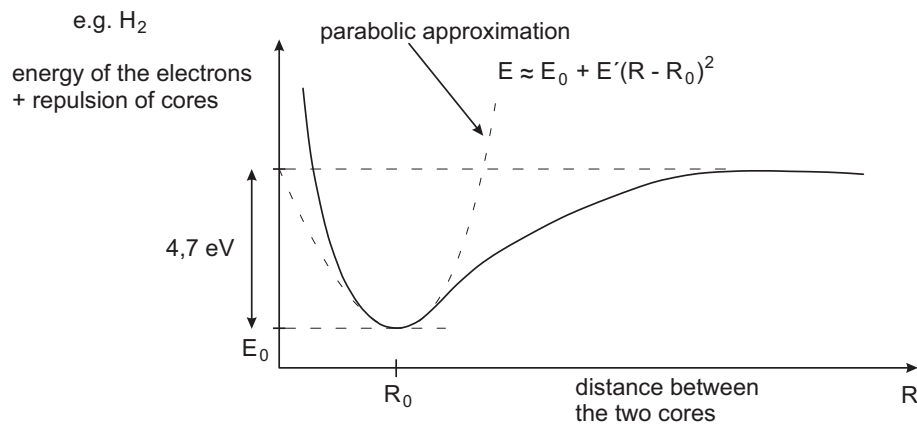
$$\hat{H}_{el} = \sum_i \left[\frac{\hat{p}_i^2}{2m_{el}} + V(\vec{r}_i) \right] + \frac{e^2}{8\pi\epsilon_0} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

(\sum_i – sum over all electrons, $V(\vec{r}_i)$ – potential defined by the cores, $\frac{e^2}{8\pi\epsilon_0} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$ – Coulomb interaction between electrons)

- energies in the eV-range (e.g. H_2 : binding energy $\Delta E = 4.7$ eV)
- defines the principal structure of spectra
- responsible for chemical bonds
- corresponding to a very fast dynamics (orbiting electrons H_2 : $T_{el} = 0.88$ fs)

b) oscillations

- electron cloud: extremely fast
- heavy cores: see an effective potential formed by the electron cloud



- cores attain a configuration corresponding to the minimum of the electron energy + energy of Coulomb repulsion of cores
- small deviations from the equilibrium position: parabolic approximation of the effective potential

⇒ harmonic oscillator

⇒ equally spaced energy levels (fine structure)

$$H_2 : \Delta E = 546 \text{ meV} \quad T_{osc} = 4.8 \text{ fs}$$

$$Na_2 : \Delta E = 3 \text{ meV} \quad T_{osc} = 1.4 \text{ ps}$$

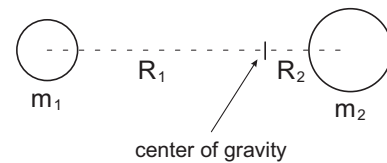
c) rotations

Molecules can rotate as a whole compound

angular momentum quantized ⇒ quantized energy levels

for two-atomic molecules (two axis of rotation equal)

- free rotation around the center of gravity



$$E_{rot} = \frac{\vec{L}^2}{2I} \quad (\vec{L}: \text{angular momentum, } I: \text{moment of inertia } I = m_1 R_1^2 + m_2 R_2^2)$$

$$\Rightarrow \text{energy levels: } E_L = \frac{\hbar^2}{2I} L[L+1]$$

$$\text{spacing: } \Delta E_L = \frac{\hbar^2}{I} L$$

not equidistant

$$\text{e.g. } H_2 : \Delta E_{L=1} = 22 \text{ meV} \quad T_{rot} = 191 \text{ fs}$$

$$Na_2 : \Delta E_{L=1} = 0.05 \text{ meV} \quad T_{rot} = 78 \text{ ps}$$

consequence

The motion of cores and of electrons happens on completely different time scales

⇒ can be considered separately

7.2 Chemical bonds

7.2.1 General remarks

covalent bonds $\hat{=}$ different cores share common electrons

two simple reasons for covalent bonds:

a) electrons shield the mutual repulsion of the cores

- already H_2^+ ($\hat{=}$ 1 electron + 2 mutually repelling protons) is stable
- simple picture
interaction energy

$$\Delta E = \frac{1}{2} \sum_i q_i \phi(\vec{r}_i) \quad q_i: \text{charge} \quad \phi: \text{potential}$$

$$\text{potential at the proton: } \phi_p = \frac{e}{4\pi\epsilon_0} \left[\frac{1}{d} - \frac{2}{d} \right] = -\frac{e}{4\pi\epsilon_0 d}$$

$$\text{potential at the electron } \phi_e = \frac{e}{4\pi\epsilon_0} \frac{4}{d}$$

total interaction energy

$$\Delta E = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \left[-\frac{2}{d} - \frac{4}{d} \right] = -\frac{3e^2}{4\pi\epsilon_0} \frac{1}{d}$$

\Rightarrow energy reduced

1 electron is enough to bind!

remark: There is an exact analytical solution for H_2^+ .

b) Electron can use many wave functions simultaneously

\Rightarrow wave function spreads over a bigger volume

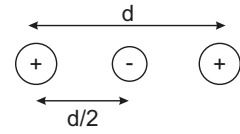
$$\Rightarrow \langle E_{\text{kin}} \rangle = \int dx \int dy \int dz \psi^*(\vec{r}) \left[-\frac{\hbar^2}{2m} \Delta \psi(\vec{r}) \right] \text{ reduced}$$

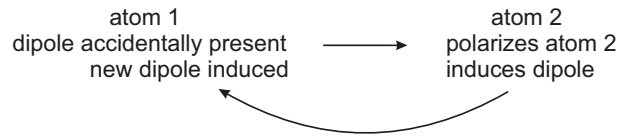
electrostatic bonds

- ion-ion bond (e.g. Na^+Cl^-)
 - electrostatic attraction
 - decays $\sim 1/d$
- ion-dipole bond
 - decay like $1/d^2$
- dipole-dipole bond
 - decay like $1/d^3$

induced dipoles (van-der-Waals interactions)

$$\text{interaction} \sim \frac{1}{d^6}$$





7.2.2 Linear Combination of Atomic Orbitals (LCAO)

here for H_2

assumption

- fixed core positions \vec{R}_a and \vec{R}_b
- wave function of the 2 electrons factorizes into a space- and spin-dependent part
 \Rightarrow spin state has no spatial dependence

$$|\psi\rangle = |\psi_R\rangle |\psi_S\rangle$$

- electrons still occupy atomic wave functions

her: 1s wave functions only

$$\phi_{a/b}(\vec{r}) = \psi_{1s}(\vec{r} - \vec{R}_{a/b}): 1s \text{ wave function centered around core } a/b$$

1. trial

$$\langle \vec{r}_1 | \langle \vec{r}_2 | \psi \rangle = \psi(\vec{r}_1, \vec{r}_2) |s\rangle$$

(\vec{r}_1 - position of electron 1, \vec{r}_2 - position of electron 2, $\psi(\vec{r}_1, \vec{r}_2)$ - space dependent part, s - spin dependent part)

$$= \phi_a(\vec{r}_1) \phi_b(\vec{r}_2) |s_1^x\rangle |s_2^y\rangle$$

($\phi_a(\vec{r}_1)$ - electron 1 on core a , $\phi_b(\vec{r}_2)$ - electron 2 on core b , $|s_1^x\rangle$ - electron 1 has spin x , $|s_2^y\rangle$ - electron 2 has spin y)

x, y can be \uparrow or \downarrow

but

Quantum mechanics requires that electrons are indistinguishable and that fermionic wave function must switch sign, when particles are interchanged.

2. trial

electrons must be present at both cores simultaneously

a) spatially symmetric wave function $|\psi\rangle_s$

$$\langle \vec{r}_1 | \langle \vec{r}_2 | \psi \rangle_s = c_s [\phi_a(\vec{r}_1) \phi_b(\vec{r}_2) + \phi_a(\vec{r}_2) \phi_b(\vec{r}_1)] \cdot [|s_1^x\rangle |s_2^y\rangle - |s_2^x\rangle |s_1^y\rangle]$$

(c_s - normalization)

what happens, if electrons are interchanged

$$\langle \vec{r}_1 | \langle \vec{r}_2 | \psi' \rangle_s = c_s [\phi_a(\vec{r}_2) \phi_b(\vec{r}_1) + \phi_a(\vec{r}_1) \phi_b(\vec{r}_2)] \cdot [|s_2^x\rangle |s_1^y\rangle - |s_1^x\rangle |s_2^y\rangle] = -\langle \vec{r}_2 | \langle \vec{r}_2 | \psi \rangle_s$$

$$([\phi_a(\vec{r}_2) \phi_b(\vec{r}_1) + \phi_a(\vec{r}_1) \phi_b(\vec{r}_2)] - \text{no change}, [|s_2^x\rangle |s_1^y\rangle - |s_1^x\rangle |s_2^y\rangle] - \text{sign changed})$$

but

spin states x and y must be different, otherwise the spin-part would vanish

\Rightarrow 2 electrons occupying a spatially symmetric wave function must have opposite spin

\Rightarrow total spin $M_s = m_{s_1} + m_{s_2} = 0$

\Rightarrow only one spin state: singlet

b) spatially antisymmetric wave function

$$\langle \vec{r}_1 | \langle \vec{r}_2 | \psi \rangle_a = c_a [\phi_a(\vec{r}_1) \phi_b(\vec{r}_2) - \phi_a(\vec{r}_2) \phi_b(\vec{r}_1)] \cdot |s\rangle_s$$

$$([\phi_a(\vec{r}_1) \phi_b(\vec{r}_2) - \phi_a(\vec{r}_2) \phi_b(\vec{r}_1)] - \text{antisymmetric}, |s\rangle_s - \text{symmetric})$$

3 possibilities for a symmetric $|s\rangle_s$

$$|s\rangle_s = \begin{cases} |\uparrow_1\rangle |\uparrow_2\rangle & m_s = 1 \\ \frac{1}{\sqrt{2}} [|\uparrow_1\rangle |\downarrow_2\rangle + |\uparrow_1\rangle |\uparrow_2\rangle] & m_s = 0 \\ |\downarrow_1\rangle |\downarrow_2\rangle & m_s = -1 \end{cases}$$

(left side: Triplet of states = projection of a state with total spin 1, right side: z -component of total spin)

expectation value of $\hat{S}^2 : \hbar^2 [L_s + 1] L_s$ with $L_s = 1$

expectation value of $\hat{S}_z : \hbar M_s$ with $-L_s \leq M_s \leq L_s$

spatially antisymmetric wave functions have parallel spins

3. calculate the total energy as function of separation of the cores

$$\hat{H} = \hat{H}_{el} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{R}_a - \vec{R}_b|}}_{\text{repulsion of the protons}}$$

energy of the bond

$$\Delta E = \underbrace{\langle \psi | \hat{H} | \psi \rangle}_{\text{expectation value}} - \underbrace{2E_{1s}}_{\text{energy of free atoms}}$$

no spin-dependent parts in \hat{H}

\Rightarrow spin neglected

now concentration on the symmetric function

$$\begin{aligned} \Delta E = & \int \psi^* \left[-\frac{\hbar^2}{2m_e} (\Delta_{\vec{r}_1} + \Delta_{\vec{r}_2}) - \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|\vec{r}_1 - \vec{R}_a|} \right. \right. \\ & \left. \left. + \frac{1}{|\vec{r}_1 - \vec{R}_b|} + \frac{1}{|\vec{r}_2 - \vec{R}_a|} + \frac{1}{|\vec{r}_2 - \vec{R}_b|} - \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right] \right] \psi \\ & \text{electrons attracted by the protons} \quad \text{mutual repulsion of electrons} \\ & -2E_{1s} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{R}_a - \vec{R}_b|} \end{aligned}$$

- simplified by employing:

$$\left[-\frac{\hbar^2}{2m_e} \Delta_{r_1} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{R}_a|} \right] \phi_a(\vec{r}_1) = E_{1s} \phi_a(\vec{r}_{1/2})$$

similar for \vec{r}_2 ϕ_b etc.

- remaining terms:

overlap of ϕ_a with potential of core $b \Rightarrow$ energy reduction

overlap of ϕ_b with potential of core $a \Rightarrow$ energy reduction

overlap of ϕ_a with ϕ_b (repulsion) \Rightarrow energy increase

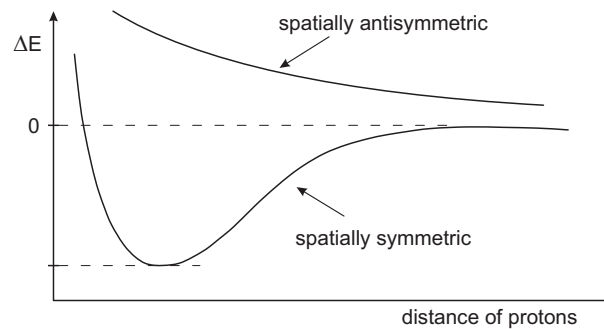
repulsion of protons \Rightarrow energy increase

e.g.

$$\int d\vec{r}_1 \int d\vec{r}_2 \phi_a(\vec{r}_1) \phi_b(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_a(\vec{r}_1) \phi_b(\vec{r}_2)$$

\vdots

result



- binding due to spatially symmetric wave-function

⇒ spins in a covalent bond are antiparallel

reason: spatially antisymmetric wave function does not allow two electrons to be on the same place

⇒ lower total electron density between the cores

⇒ lower attractive binding

but

In single atoms electrons prefer to occupy spatially antisymmetric wave functions to reduce repulsion ($\hat{=}$ parallel spins)

e.g. $7N = [\text{He}] 2s 3p \rightarrow \uparrow\uparrow\uparrow$ and not $\uparrow\downarrow\uparrow$

evaluation LCAO

- only spatial part of spatially symmetric wave function considered

- up to now: $\psi(\vec{r}_1, \vec{r}_2) = \phi_a(\vec{r}_1)\phi_b(\vec{r}_2) + \phi_a(\vec{r}_2)\phi_b(\vec{r}_1)$

⇒ binding energy $\Delta E = -3,14 \text{ eV}$ (real: $-4,75 \text{ eV}$)

1. improvement λ : determines balance between covalent and ionic bond

$$\begin{aligned} \psi(r_1, r_2) = & \left. \begin{array}{c} \begin{array}{cc} \begin{array}{c} 1 \\ - \end{array} \begin{array}{c} a \\ + \end{array} \end{array} & \begin{array}{cc} \begin{array}{c} b \\ + \end{array} \begin{array}{c} 2 \\ - \end{array} \end{array} & \begin{array}{cc} \begin{array}{c} 2 \\ - \end{array} \begin{array}{c} a \\ + \end{array} \end{array} & \begin{array}{cc} \begin{array}{c} b \\ + \end{array} \begin{array}{c} 1 \\ - \end{array} \end{array} \\ \phi_a(\vec{r}_1)\phi_b(\vec{r}_2) + \phi_a(\vec{r}_2)\phi_b(\vec{r}_1) \end{array} \right\} \text{covalent bond} \\ & + \lambda [\phi_a(\vec{r}_1)\phi_a(\vec{r}_2) + \phi_b(\vec{r}_1)\phi_b(\vec{r}_2)] \\ & \underbrace{\begin{array}{cc} \begin{array}{cc} \begin{array}{c} 1 \\ - \end{array} \begin{array}{c} a \\ + \end{array} \end{array} \begin{array}{c} b \\ + \end{array} & \begin{array}{c} a \\ + \end{array} \begin{array}{cc} \begin{array}{c} 1 \\ - \end{array} \begin{array}{c} b \\ + \end{array} \end{array} \begin{array}{c} 2 \\ - \end{array} \\ \text{ionic bond} & \quad \text{H}^- \quad \text{H}^+ \end{array}} \end{aligned}$$

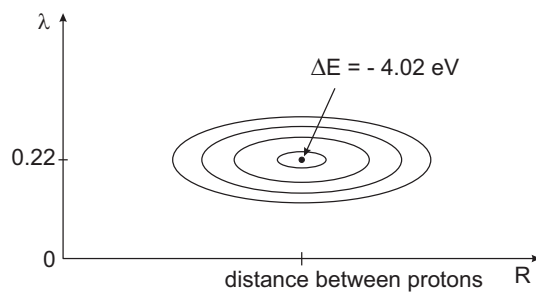
$\lambda = 0$ (Heitler-London-approximation): $\Delta E = -3,14 \text{ eV}$

$\lambda = 1$ (original LCAO): $\Delta E = -2.2 \text{ eV}$

$\psi(\vec{r}_1, \vec{r}_2) = [\phi_a(\vec{r}_1) + \phi_b(\vec{r}_1)][\phi_a(\vec{r}_2) + \phi_b(\vec{r}_2)]$ ([...] - electrons uncorrelated on both cores)

⇒ even worse

⇒ λ must be optimized simultaneously



⇒ looking for the λ with the smallest energy

2. improvement

taking into account more basis functions (not only $1s$)

taking into account 13 orbitals ⇒ $\Delta E = -4.69$

50 orbitals ⇒ $\Delta E = -4.75$

⇓

agreement within error bars of experimental values

composition of the bond:

−3.14 eV covalent bond ($\lambda = 0$)

−0.88 eV ionic bond

−0.73 eV deformation of electron wave function (= inclusion of higher orbitals)

7.3 Excited molecules

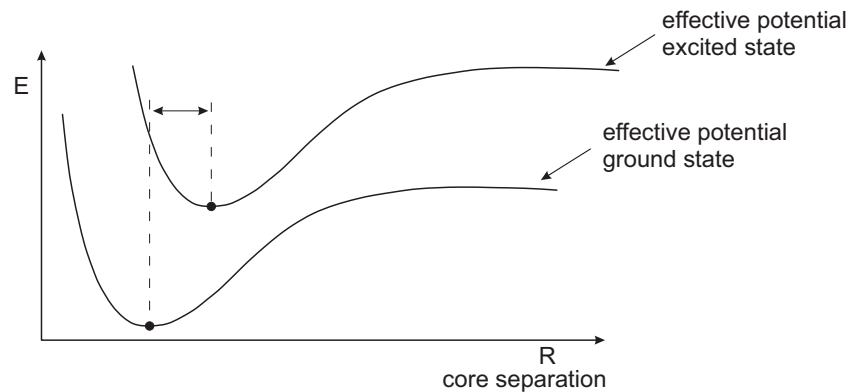
important for chemical reactions and lasers (dye lasers, excimer lasers)

7.3.1 States and transitions

- ground state of a molecule
 - only valence electrons incorporated in bonds
 - new wave functions still carry the signature of atomic wave functions
 - wave functions are filled with electrons starting with the lowest energy state
 - HOMO: highest occupied molecular orbital separated from
LUMO: lowest unoccupied molecular orbital
 - HOMO: usually a singlet state ($L_s = 0$)
 - excited state: usually a triplet state ($L_s = 1$)

but

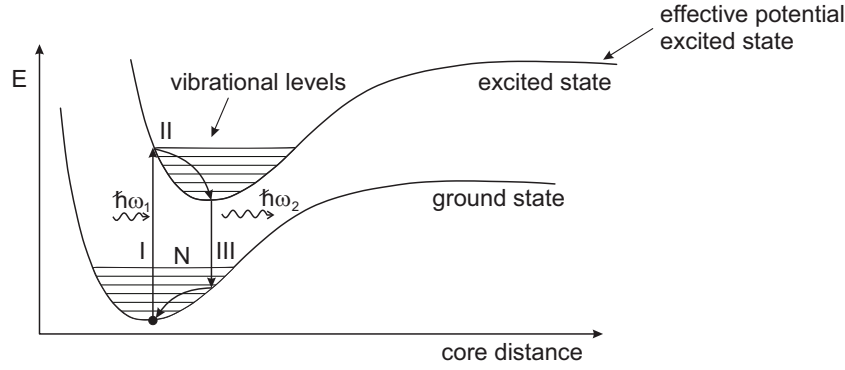
Equilibrium positions (core separations) of ground- and excited state need not match.



- excited states: usually more extended than ground state
- excited states: need not have a minimum
 - ⇒ dissociation of the molecule due to excitation

7.3.2 Optical excitations of molecules

- Optical transitions do not change the spin state
 - ⇒ transitions singlet \leftrightarrow singlet
 - triplet \rightleftharpoons triplet only
 - ⇒ The first excited state (triplet) cannot relax optically to the ground state (singlet)
 - ⇒ often a very long life time of excited states (important in chemistry)
- Born-Oppenheimer-approximation usually also applies to excited states
 - ⇒ Excited electronic states split into vibrational and rotational levels
 - optical excitation \rightleftharpoons energy jumps in eV range
 - ⇒ quasi instantaneous transitions of the electronic system
 - ⇒ core positions adapt afterwards (Franck-Condon principle)
 - typical excitation cycle
 - I: optical excitation for quasi resting cores with ω_1
 - II: cores adapt \Rightarrow excitation of vibrations
 - ⇒ vibrational relaxation to the lowest excited level



III: optical emission for quasi resting cores with $\omega_2 < \omega_1$

IV: cores adapt \Rightarrow vibrations of the ground state
 \Rightarrow relaxation to the ground state

\Rightarrow effective four level system

from chapter 5.4.

probability of an optical transition of 1 electron

$$p \sim |\langle \psi^I | \vec{r} | \psi^II \rangle|^2 = |\vec{d}|^2$$

($\langle \psi^I |$ - initial state, $\vec{r} \sim$ polarization \sim elongation, $|\psi^II \rangle$ - final state, $|\vec{d}|^2$ - dipole element)

now: many charges (electrons, cores)

$$d \sim \langle \psi^I | \sum_i q_i \vec{r}_i + \sum_j Q_j \vec{R}_j | \psi^II \rangle$$

(charges of: q_i - electrons, Q_j - cores)

As $|\psi^I \rangle$ and $|\psi^II \rangle$ must have the same spin-configuration, we only consider the spatial part in its spatial representation. Born-Oppenheimer approximation

$$\psi^{I/II}(\vec{r}_i, \vec{R}_j) = K^{I/II}(\vec{R}_j) \phi_{\vec{R}_j}^{I/II}(\vec{r}_i)$$

($K^{I/II}$ - wave function of cores, $\phi_{\vec{R}_j}^{I/II}$ - electron wave function for fixed core position)

$$\vec{d} \sim \int d\vec{R}_j \int d\vec{r}_i K^{I*}(\vec{R}_j) K^{II}(\vec{R}_j) \phi_{\vec{R}_j}^{I*}(\vec{r}_i) \phi_{\vec{R}_j}^{II}(\vec{r}_i) \left(\sum_i q_i \vec{r}_i + \sum_j Q_j \vec{R}_j \right)$$

($\int d\vec{R}_j$ - integration over all cores, more precise: $\prod_j \int d\vec{R}_j$, $\int d\vec{r}_i$ - all electrons $\prod_i \int d\vec{r}_i$)

$$\begin{aligned} \vec{d} &\sim \int d\vec{R}_j K^{I*}(\vec{R}_j) K^{II}(\vec{R}_j) \sum_j Q_j \vec{R}_j \int d\vec{r}_i \phi_{\vec{R}_j}^{I*}(\vec{r}_i) \phi_{\vec{R}_j}^{II}(\vec{r}_i) \\ &+ \int d\vec{R}_j K^{I*}(\vec{R}_j) K^{II}(\vec{R}_j) \int d\vec{r}_i \phi_{\vec{R}_j}^{I*}(\vec{r}_i) \phi_{\vec{R}_j}^{II}(\vec{r}_i) \sum_i q_i \vec{r}_i \end{aligned}$$

1. term: only non zero for $\phi^I = \phi^{II}$

\Rightarrow electronic system remains in the same state

\Rightarrow only relevant for phononic transitions

\Rightarrow here not considered

2. term: usual electronic dipole element for core position

\vec{R}_j weighted with distribution of cores

matching of core wave functions

$$\vec{d} \sim \int d\vec{R}_j \overbrace{K^{I*}(\vec{R}_j) K^{II}(\vec{R}_j)} \vec{M}_{\text{el}}(\vec{R}_j)$$

$(K^{I*}(\vec{R}_j), K^{II}(\vec{R}_j))$ - wave function of core positions in initial and final state)

with $\vec{M}_{\text{el}}(\vec{R}_j) = \int d\vec{r}_i \phi_{\vec{R}_j}^{I*}(\vec{r}_i) \phi_{\vec{R}_j}^{II}(\vec{r}_i) \vec{r}_i$

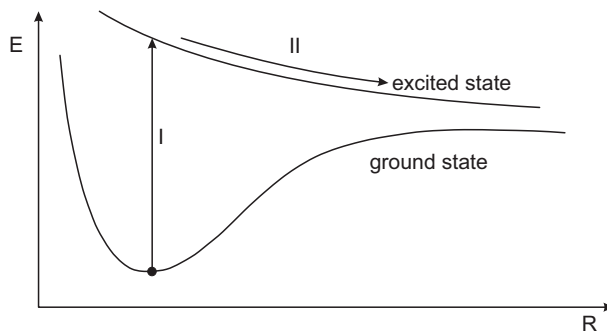
$\vec{M}_{\text{el}}(\vec{R}_j)$: dipole element for core position \vec{R}_j

- perfect material for lasers because
 - immediate inversion / no absorption of ω_2
 - \Rightarrow low threshold lasing
 - often a rather broad emission spectrum
 - \Rightarrow ultra short pulse lasers

7.3.3 Dissociation of molecules

a) optical dissociation

excited state need not have a minimum



\Rightarrow excited atoms are not bound

b) thermal dissociation

e.g. H_2 : binding energy $\Delta E = 4.75 \text{ eV}$

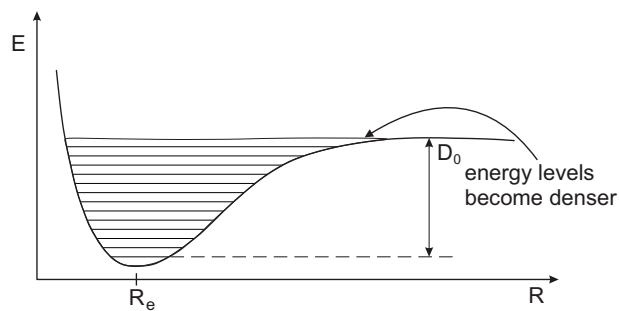
vibration quant $\Delta E = 546 \text{ meV}$

\Rightarrow only a limited number of vibration quanta can be excited (≈ 8)

\Rightarrow model of harmonic oscillator does not hold for stronger excitations

better approximation: Morse potential

$$V(R) = D_e \left(1 - e^{-a(R-R_e)} \right)^2$$



can be analytically solved

\Rightarrow only limited number of levels

dissociation for an excitation $\Delta E > D_0$

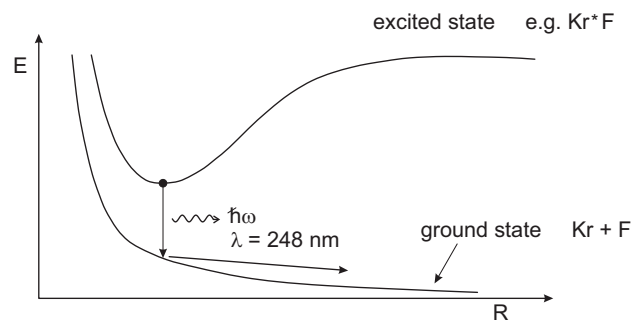
c) excimer laser

noble gases: • closed shells

• do not form molecules

excited noble gases can form molecules (excimere)

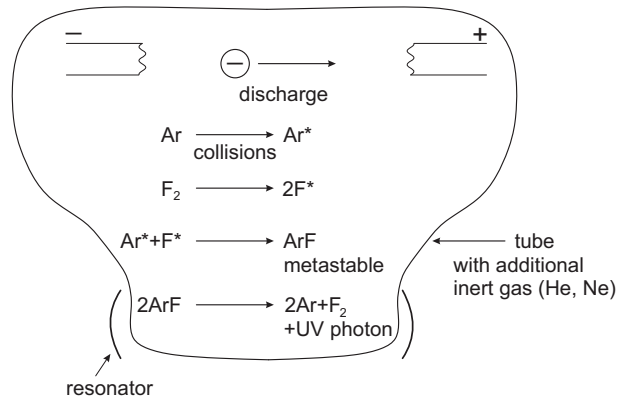
ArF, KrF, XeCl (formed by e.g. electrical discharge or electron beam)



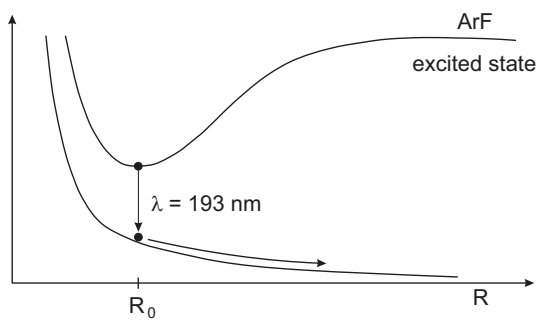
• excited molecule: formed by chemical reaction between excited atoms

- optical emission \Rightarrow decay of the molecule
- ground state never filled \Rightarrow perfect for lasers
- high excitation energies \Rightarrow UV-laser
- shortest wavelength: Ar_2 $\lambda = 126 \text{ nm}$

semiconductor lithography: ArF -laser $\lambda = 193 \text{ nm}$ (smallest structures 22 nm)



operation:



- only pulsed
- $T_P = 4 \dots 40 \text{ ns}$
- $E_P \leq 1.2 \text{ J}$
- bad optical quality
- short life time (F_2 is very reactive)

8 Radiation fields in thermal equilibrium

8.1 Thermodynamics

- each closed system: attains a thermal equilibrium
- system in thermal equilibrium:
 - has a common temperature
 - mean occupation of energy levels
$$p(E) \sim \exp\left[-\frac{E}{K_B T}\right] \text{ Boltzmann distribution}$$
$$k_B = 1.38 \cdot 10^{-23} \frac{J}{K} \text{ Boltzmann's constant}$$
e.g. 1D harmonic oscillator
 - levels: $E_n = \left(n + \frac{1}{2}\right) \hbar \omega_0$ $n = 0, 1, \dots$
 - probability to find the oscillator in thermal equilibrium in state n : $\sim \exp\left(-\frac{E_n}{k_B T}\right)$
 - mean energy per degree of freedom: $K_B T/2$ e.g. 1D harmonic oscillator

$$\begin{array}{rcccl} \text{mean energy} & = & \underbrace{\frac{1}{2} k_B T} & + & \underbrace{\frac{1}{2} k_B T} = k_B T \\ & & \text{mean kinetic energy} & & \text{mean potential energy} \end{array}$$

- radiation field in a closed system (e.g. an empty cavity)
 - attains also an equilibrium state
 - fixed spectral energy density

$$u_\omega(\omega) = \frac{\text{energy}}{\text{volume} \cdot \text{frequency interval}}$$

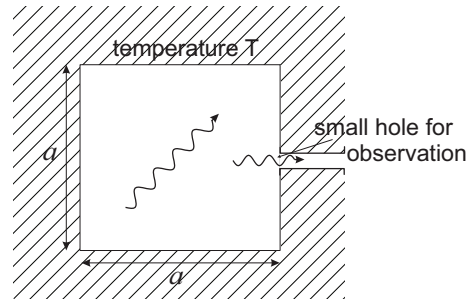
8.2 Black-body-radiation

8.2.1 Mode density

As equilibrium state does not depend on the nature of the cavity we choose the simplest one

- cube with perfectly reflecting walls

- with temperature T
- size a
- vacuum inside

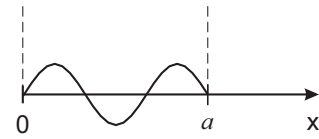


- radiation field inside the cube = standing waves

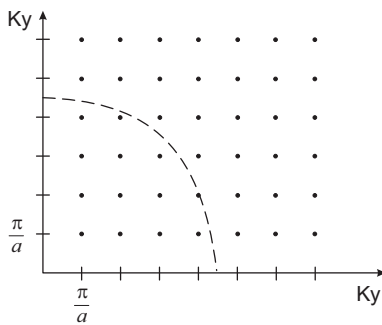
1D: $\sim \sin(k_x x)$

with $k_x = n \frac{\pi}{a}$

$n = 1, 2, 3, \dots$



3D: $\sim \sin(k_x x) \sin(k_y y) \sin(k_z z)$ with $k_i = n_i \frac{\pi}{a}$



- discrete net of possible k -value
- only positive k -values, as negative ones already incorporated in the sine function

vacuum: $|\vec{k}|^2 = \frac{\omega^2}{c^2} \Rightarrow$ strict correlation with frequency

number of modes below a certain frequency $\hat{=}$ discrete k -points within a sphere segment:

- volume in k -space per point: $V_k = [\pi/a]^3$
- 2 modes per \vec{k} -value $\hat{=}$ 2 polarizations
- $N(\omega)$: number of modes below the frequency ω

$$N(\omega) \approx 2 \frac{V_{\text{sphere segment}}}{V_K} = 2 \frac{\frac{4}{3} \pi k_{\text{max}}^3 / 8}{[\pi/a]^3}$$

with $k_{\text{max}} = \frac{\omega}{c}$

$$N(\omega) \approx \frac{1}{3\pi^2} \frac{\omega^3}{c^3} a^3$$

discretisation error

$$\begin{aligned}\frac{\Delta N}{N} &= \frac{\text{surface of sphere} \cdot \frac{\pi}{a}}{\text{volume of sphere}} \\ &= \frac{4\pi k_{\max}^2 \cdot \pi/a}{\frac{4}{3}\pi k_{\max}^3} \\ &= 3 \frac{\pi}{k_{\max} \cdot a} = \frac{3}{2} \frac{\lambda_{\min}}{a}\end{aligned}$$

\Rightarrow scales like λ_{\min}/a

\Rightarrow becomes negligible for macroscopic volumes large compared with the wavelength

modes per volume: $\frac{N(\omega)}{V} = \frac{1}{3\pi^2} \frac{\omega^3}{c^3}$

modes per volume and frequency:

$$n(\omega) = \frac{d}{d\omega} \left[\frac{N(\omega)}{V} \right] = \frac{1}{\pi^2} \frac{\omega^2}{c^3}$$

example: modes in the visible spectral range ($\lambda = 350 \text{ nm} \Rightarrow \lambda = 650 \text{ nm}$)

modes per volume = $1.65 \cdot 10^{20} \frac{\text{modes}}{\text{m}^3}$

volume per mode $\hat{=}$ cube with 182 nm size; space/mode $\sim [\text{wavelength}]^3$

8.2.2 Spectral energy density

modes: independent quantities

open question: how much energy per mode

1. trial

assumption:

1 mode = 1 degree of freedom of the radiation field

expected energy per mode: $k_B T$

$$\text{expected spectral energy density} = \frac{\text{energy}}{\text{volume} \cdot \text{frequency interval } \omega}$$

$$u_\omega(\omega) = k_B T n(\omega) = k_B T \frac{1}{\pi^2} \frac{\omega^2}{c^3}$$

\Rightarrow Rayleigh-Jeans-law

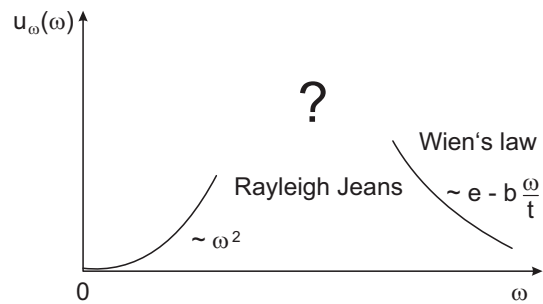
- correct for small frequencies
- wrong for high frequencies (quadratic growth): UV-disaster

2. trial

assumption:

1 mode = 1 energy level

⇒ Boltzmann distribution



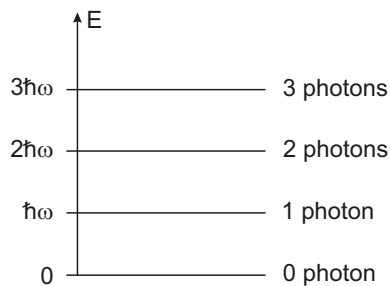
$$u_{\omega}(\omega) = \hbar \omega e^{-\frac{\hbar \omega}{k_B T}} n(\omega) = \frac{\hbar}{\pi^2} \frac{\omega^3}{c^3} e^{-\frac{\hbar \omega}{k_B T}} = a \omega^3 e^{-b \frac{\omega}{T}}$$

(a, b unknown at Wien's time)

correct for high energies (Wien's law)

3. trial Max Planck (1900), later confirmed by quantum theory

- each mode can only carry discrete amounts of energy $\hbar \omega$ (like harmonic oscillator)
- each mode has discrete and equidistant energy levels ($\hat{=}$ photons)



(quantum mechanics: already zero level has energy $\frac{1}{2} \hbar \omega$)

mean occupation of mode levels in thermal equilibrium:

$$p_n = \bar{p} e^{-n \frac{\hbar \omega}{k_B T}}$$

$\hat{=}$ probability to find the respective mode to carry n photons

The mode must be in one state.

$$1 = \sum_{n=0}^{\infty} p_n = \bar{p} \sum_{n=0}^{\infty} e^{-n \frac{\hbar \omega}{k_B T}} = \frac{\bar{p}}{1 - e^{-\frac{\hbar \omega}{k_B T}}}$$

$$\Rightarrow \bar{p} = 1 - e^{-\frac{\hbar \omega}{k_B T}}$$

mean energy per mode

$$\begin{aligned}
 \bar{E} &= \sum_{n=0}^{\infty} \hbar\omega n p_n = \hbar\omega \bar{p} \sum_{n=0}^{\infty} n e^{-n\beta} \\
 &= -\hbar\omega \bar{p} \frac{\partial}{\partial \beta} \sum_{n=0}^{\infty} e^{-n\beta} \quad \text{with } \beta = \frac{\hbar\omega}{k_B T} \\
 &= -\hbar\omega \bar{p} \frac{\partial}{\partial \beta} \frac{1}{1 - e^{-\beta}} \\
 &= +\hbar\omega \bar{p} \frac{e^{-\beta}}{[1 - e^{-\beta}]^2} \\
 &= \hbar\omega [1 - e^{-\beta}] \frac{e^{-\beta}}{[1 - e^{-\beta}]^2} = \frac{\hbar\omega}{e^{\beta} - 1}
 \end{aligned}$$

energy per frequency and volume

$$\begin{aligned}
 u_{\omega}(\omega) &= n(\omega) \bar{E}(\omega) \\
 &= \frac{1}{\pi^2} \frac{\omega^2}{c^3} \frac{\hbar\omega}{\exp[\hbar\omega/k_B T] - 1} \\
 &= \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}
 \end{aligned}$$

often expressed as energy density per frequency $f = \frac{\omega}{2\pi}$

$$u_f(f) = \frac{8\pi h f}{c^3} \frac{1}{e^{\frac{hf}{k_B T}} - 1}$$

typical numbers: room temperature $T \approx 300$ K $\Rightarrow k_B T \approx 25$ meV

optical photons $\hbar\omega \approx 2$ eV

$$\Rightarrow \hbar\omega \gg k_B T$$

$$\Rightarrow u_{\omega}(\omega) \approx \frac{\hbar\omega^3}{\pi^2 c^3} e^{-\frac{\hbar\omega}{k_B T}}$$

Thermal radiation at room temperature in the optical range obeys Wien's law and is extremely weak.

8.2.3 General rules

Although derived for radiation in a cavity the spectral shape is very general. It also applies to the spectral dependence of the radiation from hot bodies as e.g. the sun.

a) spectral maximum $\left[\frac{\partial u_{\omega}(\omega)}{\partial \omega} \right]_{\omega_M} = 0$:

$\omega_M \sim T$ - Wien's spectral displacement law \Rightarrow exercise

room temperature $T = 300$ K: $\lambda_M \approx 9.7 \mu\text{m}$

b) total energy density of the thermal radiation field

$$W = \int_0^{\infty} d\omega u_{\omega}(\omega) = a \cdot T^4$$

with $a = \frac{\pi^2 k_B^4}{15 h^3 c^3} \Rightarrow$ exercise

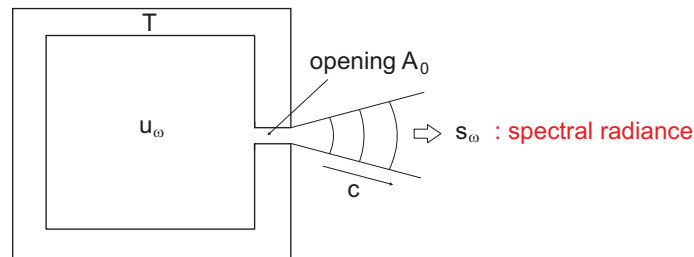
\Rightarrow importance of radiation transport grows strongly with temperature

\Rightarrow strongly temperature dependent heat capacity

$$c_{\omega} = \frac{\partial \omega}{\partial T} = 4aT^3$$

(Note: The unit of c_{ω} is $\frac{J}{m^3 K}$. A usual heat capacity has the unit $\frac{J}{kg K}$)

c) radiation



• emitted total power:

- remains constant during propagation
- propagates with the velocity of light c
- spectral radiance:

$$s_{\omega} = \frac{\text{emitted power}}{\text{solid angle} \cdot \text{area of the opening} \cdot \text{frequency interval}}$$

$$s(\omega) = \frac{1}{4\pi} c u_{\omega}(\omega)$$

($\frac{1}{4\pi}$ - total solid angle $\hat{=}$ surface area of the unit sphere, c - velocity of light, $u_{\omega}(\omega)$

- spectral energy density)

$$\text{solid angle: } d\Omega = \sin \theta d\theta d\phi \text{ with } \int_0^{\pi} d\theta \int_{-\pi}^{\pi} d\phi \sin \theta = 4\pi$$

• power per frequency received by a detector with area A directed towards the heat source for a distance r

$$P_{\omega}(\omega) = s(\omega) d\Omega = \frac{A}{r^2} A_0 \frac{\hbar \omega^3}{\pi^2 c^2} \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1}$$

($d\Omega$ - solid angle covered by detector, A - area detector, A/r^2 - solid angle, A_0 - opening)

$\varepsilon_\omega(\theta, \phi, \vec{r}, \omega, T)$: thermal emission per frequency interval $d\omega$ per area of hot body
per solid angle [$Wm^{-2}s$] depends on angle (θ, ϕ) , position \vec{r} ,
frequency ω and temperature T

$a(\theta, \phi, \vec{r}, \omega, T)$: absorption coefficient [no units], depends on angle (θ, ϕ) , position \vec{r} ,
frequency ω and temperature T

from thermal emission = absorption · spectral radiance

Kirchhoff's law

$$\frac{\varepsilon(\theta, \phi, \vec{r}, \omega, T)}{a(\theta, \phi, \vec{r}, \omega, T)} = \underbrace{\frac{1}{4\pi} c u_\omega(\omega, T) = s_\omega(\omega, T)}_{\text{no dependence on } \theta, \phi, \vec{r}}$$

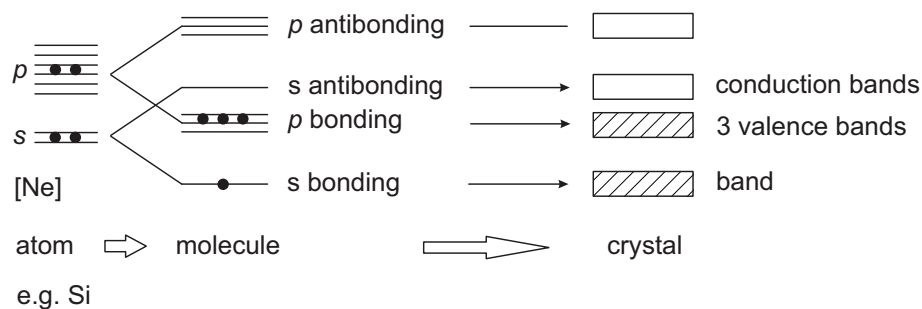
Strictly speaking an integral over the whole surface of the body must be applied. But, this relation is true for every body surrounded by thermal radiation. Hence, it must be also true locally.

consequences

- emission \sim absorption
 \Rightarrow black bodies emit stronger than white ones
- gray (no spectral dependence) and rough (no angular dependence of absorption) bodies emit with a spectral dependence similar to that of thermal radiation inside a cavity

9 Solids

- all materials (except H and He under normal pressure) form solids below a certain temperature
- state of lowest energy of many atoms: regular crystal
- most bonds:
 - electronic nature
 - valence electrons (s and p) contribute



- valence electrons shared between all atoms
 - \Rightarrow not spatially separated any more
- Pauli's principle:
 - each electron must be in a different state
 - valence electrons must be in different states with different energies
 - \Rightarrow discrete atomic levels become energy bands

9.1 The crystal lattice

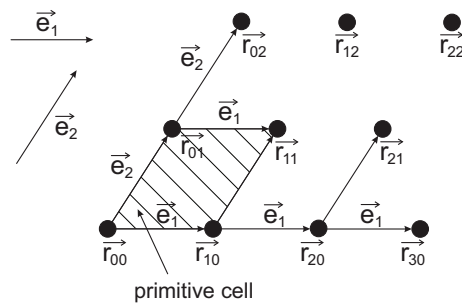
9.1.1 Real space

lattice:

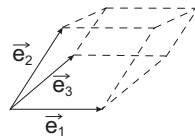
- periodic repetition of a basic structure (e.g. an atom, a molecule, ...)
- position of each basic structure: characterized by three lattice vectors \vec{e}_i ($i = 1, 2, 3$)

$$\vec{r}_{lmn} = L\vec{e}_1 + m\vec{e}_2 + n\vec{e}_3 \quad l, m, n: \text{integer}$$

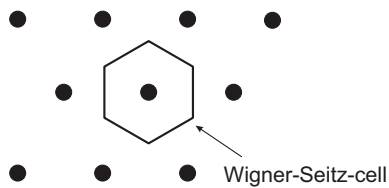
here: representation in 2D ($\hat{=}$ 2 lattice vectors)



- primitive cell:
 - built by the primitive lattice vectors
 - always a parallelepiped



- Wigner-Seitz cell: all points, which are closest to one lattice point

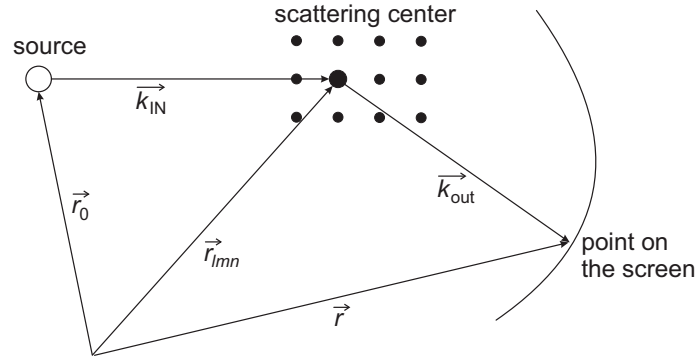


- can build up the whole lattice
- can contain several atoms

- typical lattice spacing: Si: 2 atoms per unit cell, lattice spacing: 0,54 nm

9.1.2 Wave diffraction on lattices

- determination of the structure of a lattice: scattering of a wave with short wavelength on the lattice
- waves: x -rays, neutrons, electrons ...
- here: scalar monochromatic (fixed energy / wavelength) wave with wave vector of fixed length
- configuration
- illumination with a collimated beam with fixed \vec{k}_{IN} originating from a source at \vec{r}_0



- each wave is only scattered ones at a single lattice site at \vec{r}_{lmn}
- waves from all scattering events superimpose at a point \vec{r} of the screen
- distances between source and crystal and between crystal and screen are much larger than the extension of the crystal. Therefore \vec{k}_{IN} and \vec{k}_{out} can be assumed to be the same for all lattice points contributing to a spot on the screen at \vec{r}
- elastic scattering: $|\vec{k}_{\text{out}}| = |\vec{k}_{\text{IN}}|$
- each scattering path contributes with an amplitude

$$a_{lmn} = \alpha \exp \left[i \vec{k}_{\text{IN}} (\vec{r}_{lmn} - \vec{r}_0) \right] \exp \left[i \vec{k}_{\text{out}} (\vec{r} - \vec{r}_{lmn}) \right]$$

accumulated phase = phase accumulated between source and scattering center + phase accumulated between scattering center and screen

- total amplitude on the screen

$$\begin{aligned} u(\vec{r}) &= \sum_{lmn} a_{lmn} = \alpha \sum_{lmn} e^{i \vec{k}_{\text{IN}} (\vec{r}_{lmn} - \vec{r}_0)} e^{i \vec{k}_{\text{out}} (\vec{r} - \vec{r}_{lmn})} \\ &= \alpha e^{i (\vec{k}_{\text{out}} \vec{r} - \vec{k}_{\text{IN}} \vec{r}_0)} \underbrace{\sum_{lmn} e^{-i \Delta \vec{k} \vec{r}_{lmn}}}_{\text{Fourier transformation}} \end{aligned}$$

of the lattice with respect to $\Delta \vec{k}$

with $\Delta \vec{k} = \vec{k}_{\text{out}} - \vec{k}_{\text{IN}}$

$$u(\vec{r}) = \underbrace{\alpha e^{i\phi} \sum_{lmn} e^{-i \Delta \vec{k} [l \vec{e}_1 + m \vec{e}_2 + n \vec{e}_3]}}_{\text{unimportant}}$$

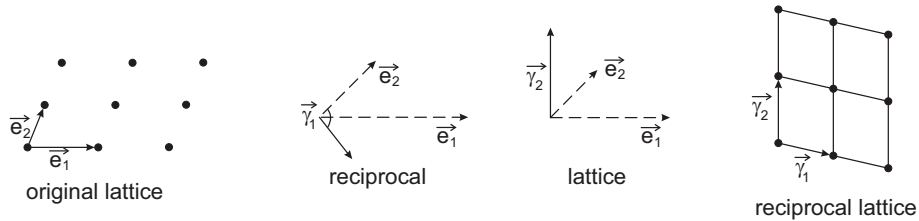
unimportant

\sum_{lmn} only growths, if $\Delta\vec{k}\vec{e}_i = g_i \cdot 2\pi$ with g_i integer

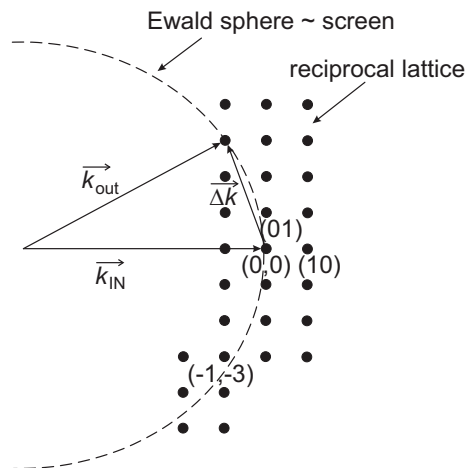
$\Rightarrow \Delta\vec{k}$ must belong to the reciprocal lattice

$$\Delta\vec{k} = \sum_{i=1}^3 g_i \vec{\gamma}_i \text{ with } \vec{\gamma}_i \cdot \vec{e}_j = 2\pi\delta_{ij}$$

reciprocal lattice = Fourier transform of the original lattice



geometrical visualization of scattering



To observe a bright spot on the screen (constructive interference) $\Delta\vec{k}$ must be an element of the reciprocal lattice or the Ewald sphere must hit a point of the reciprocal lattice

spots on the screen = farfield pattern

= cut through the Fourier transform of the object (here reciprocal lattice) with the Ewald sphere (also applicable to microscopy of 3d transparent objects)

to increase the probability to hit a point of the reciprocal lattice:

- using many rotated crystals (Debye Scherer method: good to measure lattice constants) \Rightarrow concentric circles on the screen
- using nonmonochromatic waves (Laue method: good to determine the crystal symmetry)

9.2 Electrons in lattices

valence electrons:

- "see" a periodic potential formed by the cores and by inner electrons
- experience the interaction with other electrons
 \Rightarrow not considered here

now: eigenfunctions and energies of periodic potentials

9.2.1 Bloch's Theorem

Hamiltonian: $\hat{H} = -\frac{\hbar^2}{2m}\Delta + V(\vec{r})$ with the periodic potential $V(\vec{r} + l\vec{e}_1 + m\vec{e}_2 + n\vec{e}_3) = V(\vec{r})$

- translation operator: $\hat{T}_{lmn}f(\vec{r}) = f(\vec{r}) = f(\vec{r} + l\vec{e}_1 + m\vec{e}_2 + n\vec{e}_3)$

$$\underbrace{\hspace{10em}}_{\vec{r}_{lmn}}$$

as $V(\vec{r})$ is periodic: $[\hat{T}_{lmn}, \hat{H}] = 0$

$\Rightarrow \hat{T}_{lmn}$ and \hat{H} must have common eigenfunctions

- eigenfunctions of \hat{T}_{lmn} : $\hat{T}_{lmn}f_\lambda(\vec{r}) = \lambda f_\lambda(\vec{r}) = f_\lambda(\vec{r} + \vec{r}_{lmn})$
 - translations of f_λ result in multiplication with λ
 \Rightarrow exponential growth with $|\lambda|^n$ for n translations
 - $|\lambda| = 1$ must hold that f can be normalized

Remark: As f is defined on an infinite area A either a so-called δ -normalization must be applied or A must be artificially limited to finite, but arbitrarily large size with periodic boundary conditions. In both cases exponential growth of $f_\lambda(\vec{r})$ is prohibited

- eigenfunctions of \hat{T}_{lmn} have the form $f_\lambda(\vec{r} + \vec{r}_{lmn}) = e^{i\phi_\lambda} f(\vec{r})$
- because all translational operators commute and are additive ($\hat{T}_{lmn}\hat{T}_{l'm'n'} = \hat{T}_{l+l', m+m', n+n'}$) they must have a joint eigenfunction system $f_{\vec{k}}(\vec{r})$ of the form

$$\hat{T}_{lmn}f_{\vec{k}}(\vec{r}) = \exp[i\vec{k}\vec{r}_{lmn}]f_{\vec{k}}(\vec{r}) = f_{\vec{k}}(\vec{r} + \vec{r}_{lmn})$$

$$\Rightarrow f_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{i\vec{k}\vec{r}} \text{ with } u_{\vec{k}}(\vec{r}) \text{ lattice periodic } u_{\vec{k}}(\vec{r} + \vec{r}_{lmn}) = u_{\vec{k}}(\vec{r})$$

$$\vec{k} \text{ can be decomposed } \vec{k} = \vec{k}_B + \sum_{i=1}^3 a_i \vec{\gamma}_i \quad a_i: \text{ integer}$$

$$\vec{\gamma}_i: \text{ vector of reciprocal lattice with } \vec{\gamma}_i \vec{e}_j = 2\pi\delta_{ij}$$

a_i chosen such, that \vec{k}_B belongs to the Wigner-Seitz cell of the reciprocal lattice (first

Brillouin zone)

\vec{k}_B : Bloch vector

$$\begin{aligned}
 f_{\vec{k}}(\vec{r}) &= \underbrace{u_{\vec{k}}(\vec{r})}_{\text{also lattice periodic as } u_{\vec{k}}(\vec{r} + \vec{r}_{lmn})} e^{i \sum_{i=1}^3 a_i \vec{\gamma}_i \vec{r}} \underbrace{e^{i \vec{k}_B \vec{r}}}_{\text{multiple of } 2\pi} \\
 &= \underbrace{u'_{\vec{k}}(\vec{r})}_{\text{lattice periodic}} e^{i \vec{k}_B \vec{r}}
 \end{aligned}$$

– as translational operators and \hat{H} share the same eigenfunction system:

Bloch theorem: The eigenfunctions of \hat{H} in a periodic lattice have the form $\psi(\vec{r}) = u(\vec{r})e^{i\vec{k}_B\vec{r}}$, where $u(\vec{r})$ is a lattice periodic function and \vec{k}_B an element of the first Brillouin zone.

consequences:

Eigenstates of a lattice can be chosen such, that these electrons occupying eigenstates of a lattices have a lattice periodic probability density $|\psi(\vec{r} + \vec{r}_{lmn})|^2 = |\psi(\vec{r})|^2$

9.2.2 Band structure

\vec{k}_B : characterizes solution

a) free particle in 1D

- 1d-lattice with period a:

Wigner-Seitz cell $-\frac{a}{2} \leq x \leq \frac{a}{2}$

length of lattice vector: $|\vec{e}_1| = a$

- reciprocal lattice

1st Brillouin zone

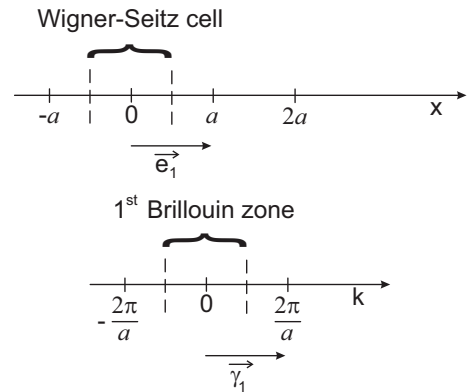
$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$$

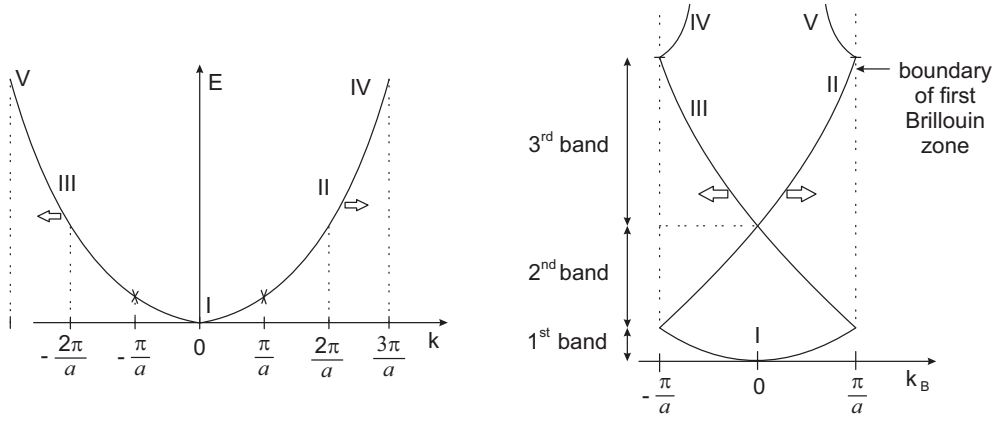
length of lattice vector $|\vec{\gamma}_1| = \frac{2\pi}{a}$

- free particle: $\psi(x) = e^{ikx}$ with energy $E = \frac{\hbar^2 k^2}{2m}$

\Rightarrow corresponding Bloch vector: $k_B = k - g \frac{2\pi}{a}$

g integer and chosen such that $-\frac{\pi}{a} \leq k_B \leq \frac{\pi}{a}$ holds





1st band: $\psi(x) = u_{k_B}(x)e^{ik_B x}$ $u_{k_B}(x) = 1$

2nd and 3rd band: $\psi(x) = u_{k_B}(x)e^{ik_B x}$

section II: $u_{k_B}(x) = e^{2i\frac{\pi}{a}x}$ $k_B = k - \frac{2\pi}{a}$ $-\frac{\pi}{a} \leq k_B \leq \frac{\pi}{a}$ $k > \frac{\pi}{a}$

section III: $u_{k_B}(x) = e^{-2i\frac{\pi}{a}x}$ $k_B = k + \frac{2\pi}{a}$ $k < -\frac{\pi}{a}$