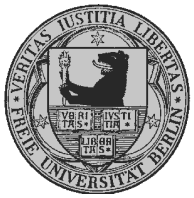
Physics of Atoms and Molecules

Prof. K. Heyne



Inhalt

1 Introduction

The first speculations on the atomic nature of matter was made by Greek philosophers such as Anaxagoras (500-428 BC), Empedocles (484-424 BC), Leucippus (450 BC) and Democritus (460-370 BC) arguing that the universe consists of empty space and indivisible atoms. Aristotele (384-322 BC), however rejected the atomic hypothesis and strongly supported the concept of the continuity of matter.

This question was re-opened following the experimental discovery of gas laws by R. Boyle in 1662, the interpretation of these laws by D. Bernoulli in 1738, and the development of the kinetic theory of gases throughout the nineteenth century by R. Clausius, J.C. Maxwell and L. Boltzmann. In parallel laws of chemical combination were being discovered, such as the law of definite proportions (by J.L. Proust in 1801) and the law of multiple proportions (by J. Dalton in 1807), supporting the concept of the atomic nature of matter. During the following years elementary units and physical constants were determined strongly related to the atomic nature of matter:

- **Avogadro's Number** $N_A = 6.02214 \cdot 10^{23} \frac{1}{mol}$ is the number of atoms or molecules in one mole of any substance. A mole is defined as the quantity of ^{12}C weighing $\mu = 12$ grams, where μ is the atomic or molecular weight of the substance.

- **Faraday's constant** $F = 9.64853 \cdot 10^4 \frac{C}{mol}$ defines the existence of the elementary unit of electricity. Faraday's laws of electrolysis, which can be summarized by the formula,

  $$M = \frac{Q}{F}\frac{\mu}{\upsilon}$$

  where Q is the quantity of electricity and υ the valency, demonstrate that it takes 96484.3 C to liberate for example 1.008 g of hydrogen, 35.5 g of chlorine and 8 g of oxygen.

- **Specific charge** $\frac{e}{m_e} = 1.75881962 \cdot 10^{11} \frac{C}{kg}$ of an cathode ray measured in Thomson's experiment (in 1897), where e is the natural unit of electricity and m_e is its mass. The specific charge for the lightest known positive ion (the hydrogen ion) is smaller by a factor of approximately 1840, so either the cathode ray particles are much lighter or they carry a very large charge.

- **The charge of the electron** was measured in Millikan's experiment to be $e = 1.6021773 \cdot 10^{-19} C$. Combining these results with the value of $\frac{e}{m_e}$, a value for the mass of the electron is obtained $m_e = 9.1093897 \cdot 10^{-31} kg$.

During the later part of the nineteenth century, and in the early years of the twentieth century, evidence accumulated that classical physics, i.e. Newton's laws of motion and Maxwell's electromagnetic equations, are inadequate to describe atomic phenomena. Most striking is the atomic or molecular picture of a number of electrons moving and accelerating around an attracting nucleus, similar to the planets circling around the sun in the solar system. This picture is in direct contradiction to the stability of atoms and molecules, since accelerating charges would continuously loose energy by emitting electromagnetic radiation, as a result of Maxwell's equations:

$$\vec{\nabla} \bullet \vec{B} = 0 \tag{1.1}$$

$$\vec{\nabla} \times \vec{E} + \frac{\partial}{\partial t}\vec{B} = 0 \tag{1.2}$$

$$\vec{\nabla} \bullet \vec{D} = \varrho \tag{1.3}$$

$$\vec{\nabla} \times \vec{H} - \frac{\partial}{\partial t}\vec{D} = \vec{j} \tag{1.4}$$

with relations in homogeneous and linear media:

$$\vec{B} = \mu_0(\vec{H} + \vec{M}) \rightarrow \mu_r \mu_0 \vec{H} \tag{1.5}$$

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} \rightarrow \varepsilon_r \varepsilon_0 \vec{E} \tag{1.6}$$

Electromagnetic radiation from decelerated electrons can be observed for example in the bremsstrahlung and one of the most powerful light sources available make use of highly accelerated charged particles to generate broadband electromagnetic radiation from the ultraviolet to the near infrared spectral range (**F**ree **e**lectron **l**aser in Fig. 1, BESSY in, Fig. 1).

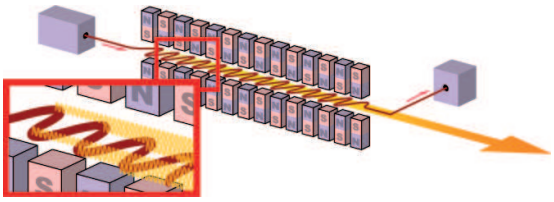


Abbildung 1.1. Light generation in a free electron laser. Note, that the lasing process is due to stimulated emission in the direction of the moving electrons.

1.1 Planck's energy distribution law

The first clues to a new physics, based on the quantisation of energy, came from a study of the properties of radiation from hot bodies. In 1879, J. Stefan showed

Abbildung 1.2. Top view of the electron synchrotron BESSY in Berlin-Adlershof. The electrons stored on circular orbits move with relativistic velocities, emitting continuously synchrotron radiation.

that the total power emitted per unit area, R, called the total emissive power (or total emittance) from a body at the absolute temperature T could be represented by the empirical law

$$R = \epsilon\sigma T^4 \tag{1.7}$$

where ϵ is called the emissivity with $\epsilon \leq 1$. The emissivity, ϵ, varies with the nature of the surface, and $\sigma = 5.67 \cdot 10^{-8} \frac{W}{m^2 \cdot K^4}$ is known as Stefan's constant. The spectral distribution of the emitted light depends strongly on the temperature (Fig. 1.1) and exhibits a maximum value at wavelength λ_{max} following the Wien's displacement law, with $b = 2.898 \cdot 10^{-3} mK$:

$$\lambda_{max} T = b \tag{1.8}$$

When a body is in thermal equilibrium with its surroundings, and therefore is at constant temperature, it must absorb and emit the same amount of radiant energy per time. Analogue to the emissivity, absorptivity, a, is defined as the fraction of the absorbed radiant energy falling on the surface. A body having an absorptivity equal to unity is called black body. A close approximation to a black body is an enclosed cavity with blackened interior walls containing a

small hole. Radiation that enters the hole has very little chance of escaping. If the inside of this cavity is in thermal equilibrium it must emit as much energy as it absorbs (on every time scale) and the emission from the hole is therefore characteristic of the equilibrium temperature T inside the cavity. This type of radiation is called thermal radiation. In the latter part of the nineteenth century

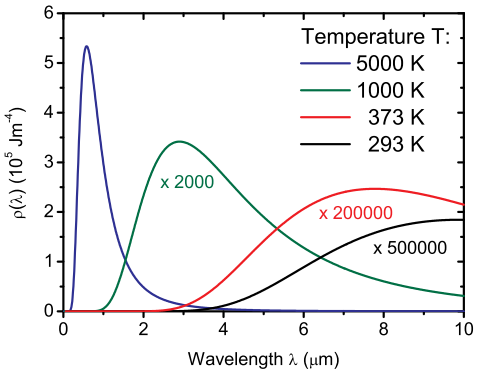


Abbildung 1.3. Energy density per unit volume and wavelength as a function of wavelength in μm for different temperatures T.

experimental measurements of this spectral profile had already been obtained and fitted to an empirical formula. Attempts to explain the data were based on treating the electromagnetic radiation as a collection of oscillators, each oscillator with its own characteristic frequency. The problem was to determine how many oscillations at a given frequency could be fitted inside a cavity. For convenience purposes, we choose cartesian coordinates and a cubical cavity with sides of length L. A plane electromagnetic standing wave $e^{i\vec{k}\bullet\vec{r}}$ has to satisfy the (periodic) boundary conditions inside this cavity

$$e^{ik_x x} = e^{ik_x(x+L)}; \quad \text{and} \quad A(0) = A(L) = 0 \tag{1.9}$$

with similar equations for the y and z components of the wave. Equation 1.9 is satisfied if

$$k_\jmath = \frac{2\pi\ell}{L} \tag{1.10}$$

where $\jmath = \{x, y, z\}$ and $k_\jmath$ are the components of the wave vector $\vec{k}$ of the oscillation and ℓ are integers.

$$\vec{k} = |\vec{k}|\,\mathbf{k} = \frac{\omega}{c}\,\mathbf{k} = \frac{2\pi}{\lambda}\,\mathbf{k} \tag{1.11}$$

This means for a single component the wavelength has to be $\lambda_\jmath = \frac{L}{\ell}$ or $k_\jmath = \frac{2\pi\ell}{L}$. In the three-dimensional $\vec{k}$-space, whose axes are k_x, k_y, and k_z the possible $k_\jmath$

values in the volume L^3 satisfying equation 1.10 form a lattice with size of a unit cell of $(\frac{2\pi}{L})^3$. The spacing of adjacent modes in the k_j direction is $\frac{2\pi}{L}$ and the permitted k_j values are 0, $\frac{2\pi}{L}$, $\frac{4\pi}{L}$, *etc.*, correspond to oscillation wavelengths ∞, L, $\frac{L}{2}$, *etc.* The total number of modes of oscillation with $|\overrightarrow{k}| \leq k$ ($|\overrightarrow{k}|$-radius in a sphere) and two distinct polarizations of the radiation field is

$$\begin{aligned} N_k &= 2 \times \frac{volume\, of\, \overrightarrow{k}\, -\, space}{volume\, of\, unit\, cell} \\ &= 2 \times \frac{4}{3}\pi k^3 \times (\frac{L}{2\pi})^3 \qquad (1.12) \\ &= \frac{k^3 L^3}{3\pi^2} \qquad (1.13) \end{aligned}$$

Since $k = \frac{2\pi\nu}{c}$ the total number of frequencies $\leq \nu$ in the volume $V = L^3$ is

$$N_\nu = \frac{8\pi\nu^3 L^3}{3c^3} = \frac{8\pi\nu^3 V}{3c^3} \qquad (1.14)$$

The mode-density, which is the number of modes per unit volume and unit frequency interval is

$$\widehat{p}(\nu) = \frac{1}{V}\frac{dN_\nu(\nu)}{d\nu} = \frac{8\pi\nu^2}{c^3} \qquad (1.15)$$

Rayleigh and Jeans used this type of mode-density to describe the spectral composition of black-body radiation by calculating the energy density

$$p(\nu) = \frac{8\pi\nu^2}{c^3}\overline{\varepsilon} \qquad (1.16)$$

where $\overline{\varepsilon}$ is the average energy in the mode with frequency ν. The energy ε of each oscillator can take any value, independently of the frequency ν, but since the system is in thermal equilibrium, the average energy $\overline{\varepsilon}$ can be obtained by weighting each value of ε with the Boltzmann factor $\exp(-\varepsilon/(k_B T))$, where $k_B = 1.380658 \times 10^{-23} JK^{-1}$ is Boltzmann's constant. With $\beta = \frac{1}{k_B T}$ we have

$$\begin{aligned} \overline{\varepsilon} &= \frac{\int_0^\infty \varepsilon e^{-\beta\varepsilon} d\varepsilon}{\int_0^\infty e^{-\beta\varepsilon} d\varepsilon} \qquad (1.17) \\ &= -\frac{d}{d\beta}[ln \int_0^\infty e^{-\beta\varepsilon} d\varepsilon] = \frac{1}{\beta} = k_B T \qquad (1.18) \end{aligned}$$

Inserting this value of $\overline{\varepsilon}$ into (1.16) gives the Rayleigh-Jeans distribution law

$$p(\nu) = \frac{8\pi\nu^2}{c^3} k_B T \qquad (1.19)$$

In the limit of long wavelengths the Rayleigh-Jeans result approaches the experimental results. However, $p(\nu)$ does not show the observed maximum, and diverges

as $\nu \to \infty$. This behaviour at short wavelengths is known as the 'ultra-violet catastrophe'. Planck resolved these difficulties with his quantum hypothesis. He proposed that each oscillation mode could only take certain quantized energies

$$E_{n_v} = (n + \frac{1}{2})h\nu, \qquad n = 0, 1, 2, 3 \ldots, \tag{1.20}$$

where the contribution $\frac{1}{2}h\nu$ is called the zero point energy, with the Planck's constant $h = 6.6260755 \times 10^{-34} Js$. The probability of finding energy E_n in a particular mode of oscillation is given by classical Maxwell-Boltzmann statistics (integration over the energy is not longer possible), i.e.,

$$\frac{P(n)}{P(0)} = \frac{e^{\frac{-E_n}{k_B T}}}{e^{\frac{-E_0}{k_B T}}} = e^{\frac{-nhv}{k_B T}} \tag{1.21}$$

where P(n)and P(0) are the probabilities of finding the energy E_n and the lowest energy E_0 in the mode. The average energy $\overline{E_\nu}$ of a mode ν is now given by:

$$\overline{E_\nu} = \sum_{n=0}^{\infty} P(n)E_n = \sum_{n=0}^{\infty} P(0)e^{\frac{-nh\nu}{k_B T}}(n + \frac{1}{2})h\nu \tag{1.22}$$

Now, if a particular oscillation is excited it must be in one of the quantized states, therefore the normalization relation holds

$$\sum_{n=0}^{\infty} P(n) = 1 \tag{1.23}$$

$$\sum_{n=0}^{\infty} P(0)e^{\frac{-nh\nu}{k_B T}} = 1 \tag{1.24}$$

$$\Rightarrow P(0) = \frac{P(n)}{e^{\frac{-nh\nu}{k_B T}}} \tag{1.25}$$

$$\frac{1}{P(0)} \sum_{n=0}^{\infty} P(n) = \sum_{n=0}^{\infty} e^{\frac{-nh\nu}{k_B T}} \tag{1.26}$$

$$\Rightarrow P(0) = \frac{\sum_{n=0}^{\infty} P(n)}{\sum_{n=0}^{\infty} e^{\frac{-nh\nu}{k_B T}}} \tag{1.27}$$

$$\Rightarrow P(0) = \frac{1}{\sum_{n=0}^{\infty} e^{\frac{-nh\nu}{k_B T}}} \tag{1.28}$$

This gives

$$\overline{E_\nu} = \frac{\sum_{n=0}^{\infty}(n+\frac{1}{2})h\nu e^{\frac{-nh\nu}{k_BT}}}{\sum_{n=0}^{\infty} e^{\frac{-nh\nu}{k_BT}}} \tag{1.29}$$

$$= \frac{1}{2}h\nu + \frac{h\nu e^{\frac{-h\nu}{k_BT}} + 2h\nu e^{\frac{-2h\nu}{k_BT}} + \cdots + nh\nu e^{\frac{-nh\nu}{k_BT}}}{1 + e^{\frac{-h\nu}{k_BT}} + e^{\frac{-2h\nu}{k_BT}} + \cdots + e^{\frac{-nh\nu}{k_BT}}} \tag{1.30}$$

$$= \frac{1}{2}h\nu - \frac{\frac{d}{d(1/k_BT)}(e^{\frac{-h\nu}{k_BT}} + e^{\frac{-2h\nu}{k_BT}} + \cdots)}{\frac{1}{(1-e^{\frac{-h\nu}{k_BT}})}} \tag{1.31}$$

$$= \frac{1}{2}h\nu - \frac{\frac{d}{d(1/k_BT)}[\frac{1}{1-e^{\frac{-h\nu}{k_BT}}}]}{\frac{1}{(1-e^{\frac{-h\nu}{k_BT}})}} \tag{1.32}$$

$$= \frac{1}{2}h\nu - \frac{\frac{d}{d\beta}(1-e^{-\beta h\nu})^{-1}}{(1-e^{-\beta h\nu})^{-1}} \tag{1.33}$$

$$= \frac{1}{2}h\nu + \frac{(1-e^{-\beta h\nu})^{-2} \times h\nu e^{-\beta h\nu}}{(1-e^{-\beta h\nu})^{-1}} \tag{1.34}$$

$$= \frac{1}{2}h\nu + \frac{h\nu e^{-\beta h\nu}}{(1-e^{-\beta h\nu})} \tag{1.35}$$

$$\overline{E_\nu} = \frac{1}{2}h\nu + \frac{h\nu}{e^{\beta h\nu}-1} \tag{1.36}$$

Here, we used the mathematical 'trick' that the series in the numerator is the derivative of a geometric series that we can sum easily. Another way to derive the formula is:

$$\bar{\varepsilon} = \frac{\sum_{n=0}^{\infty}(n+\frac{1}{2})\varepsilon_0 e^{-\beta n\varepsilon_0}}{\sum_{n=0}^{\infty} e^{-\beta n\varepsilon_0}} = \frac{1}{2}\varepsilon_0 - \frac{d}{d\beta}[ln\sum_{n=0}^{\infty} e^{-\beta n\varepsilon_0}] \tag{1.37}$$

$$= \frac{1}{2}\varepsilon_0 - \frac{d}{d\beta}[ln(\frac{1}{1-e^{-\beta\varepsilon_0}})] = \varepsilon_0[\frac{1}{2} + \frac{1}{e^{\beta\varepsilon_0}-1}] \tag{1.38}$$

Here, we used $\varepsilon_0 = h\nu$. Substituting the value of $\bar{\varepsilon}$ in (1.16), we find

$$p(\nu) = \frac{8\pi\nu^2}{c^3}(h\nu[\frac{1}{2} + \frac{1}{e^{\beta h\nu}-1}]) \tag{1.39}$$

The factor $\frac{1}{2}$ comes from zero point energy that cannot be released, so the available stored energy in the field is given by Planck's distribution law:

$$p(\nu) = \frac{8\pi h\nu^3}{c^3}[\frac{1}{e^{\frac{h\nu}{k_BT}}-1}] \tag{1.40}$$

This is (the number of modes per volume per frequency interval) x (photon energy) x $1/(e^{h\nu/k_BT}-1)$. The quantity $1/(e^{h\nu/k_BT}-1)$ represents the average number of photons in each mode. This is called the *occupation number* of the modes of the field.

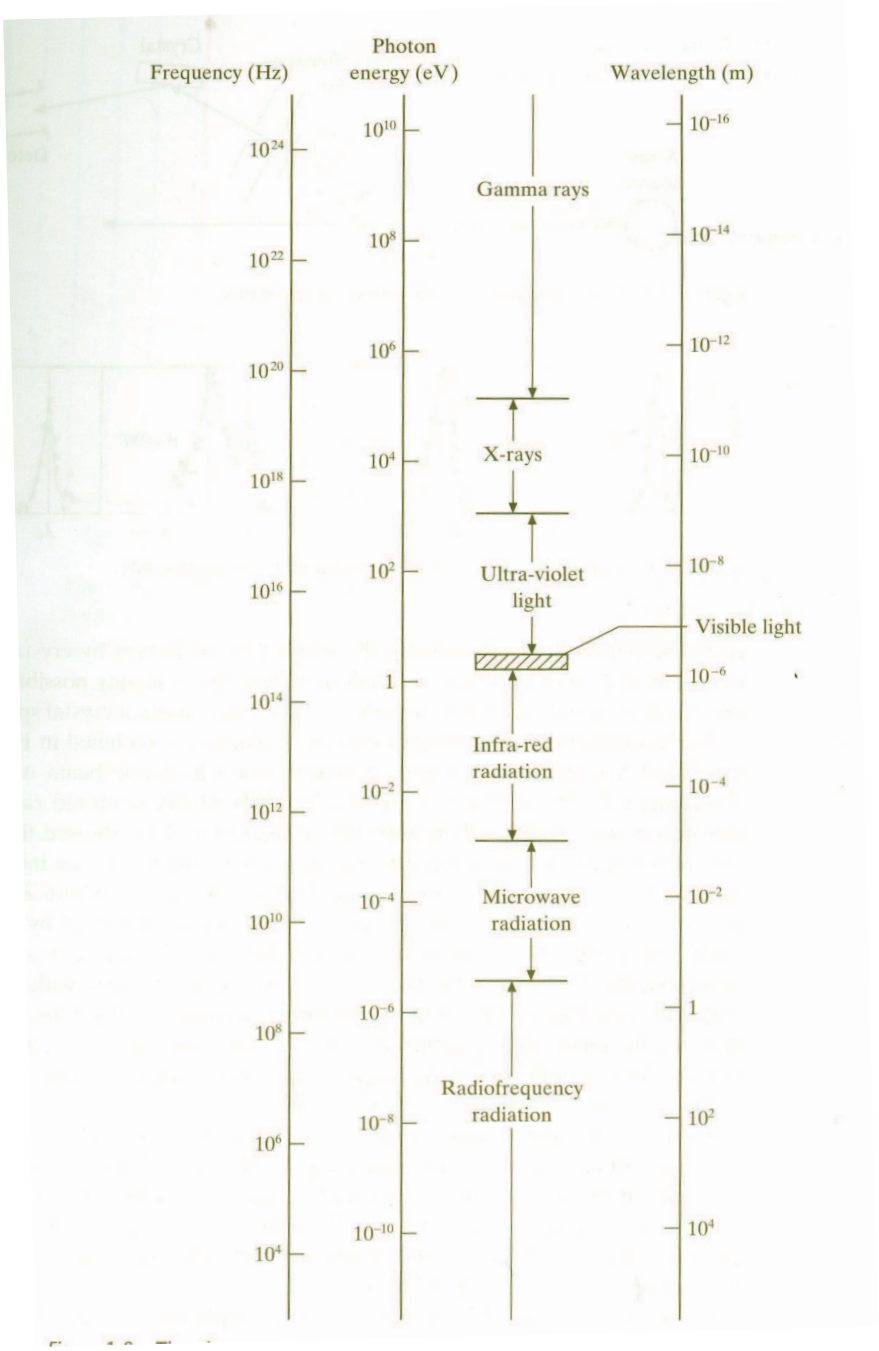


Abbildung 1.4. Frequency ranges in different units.

1.2 Radiative transitions in a two level system

Consider molecules with discrete energy levels shown schematically in Fig. (1.2). Transitions of electrons from one level to the other can occur in three ways: Spontaneous emission, stimulated emission and stimulated absorption.

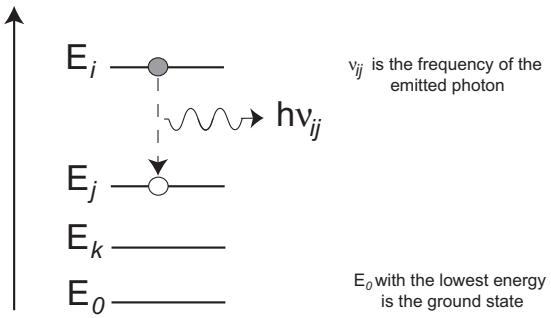


Abbildung 1.5. Energy levels of a particle (atom, molecule, etc.). Radiative transitions can occur between different energy levels upon absorbing or emitting photons.

1.2.1 Spontaneus Emission

An electron spontaneously undergoes a transition from a higher (occupied) energy level E_i to a lower (unoccupied) one E_j as shown in Fig. (1.2.2). The released energy is emitted by a photon of frequency

$$\nu_{ij} = \frac{E_i - E_j}{h} \tag{1.41}$$

This photon is emitted in a random direction with arbitrary polarization in the absence of magnetic and electric fields. The photon carries away momentum

$$\overrightarrow{p} = \frac{h\overrightarrow{k}}{2\pi} = \hbar\overrightarrow{k} = \frac{h}{\lambda}\mathbf{k} \tag{1.42}$$

$$|p| = \frac{h}{\lambda} = \frac{h\nu}{c} \tag{1.43}$$

and the emitting particle (atom, molecule, ion, etc.) recoils in the opposite direction. The probability of the spontaneous emission process is given quantitatively by the Einstein coefficient A_{ij} defined as the probability per second of a spontaneous transition from level i to level j. If the population density per unit volume in the level i is N_i then $N_i A_{ij}$ is the probability per second and unit volume for a transition from level i to level j ($i \to j$). The total rate at which spontaneous radiative transitions are made between the two levels is

$$\frac{dN_i}{dt} = -N_i A_{ij} \tag{1.44}$$

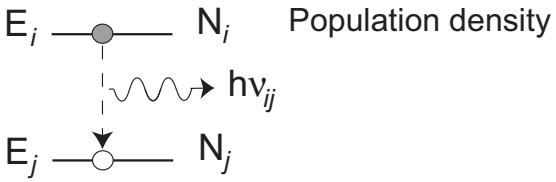


Abbildung 1.6. Transition from a higher energy i level to a lower energy level j by light emission.

The negative sign indicates that the population of the upper level is decreasing. Generally the transition of an electron can occur to more than one unoccupied lower level, unless it is in the first (lowest) excited level. The total transition rate for transitions from level i is $A_i\, s^{-1}$ where

$$A_i = \sum_j A_{ij} \tag{1.45}$$

The summation runs over all levels j lower in energy than the level i and the total rate at which the population of level i changes by spontaneous emission is

$$\frac{dN_i}{dt} = -N_i A_i \qquad \Rightarrow \qquad N_i = constant \times e^{-A_i t} \tag{1.46}$$

with $t = 0$ and $N_i = N_i^0$ it is

$$N_i = N_i^0 e^{-A_i t}. \tag{1.47}$$

The population N_i of the level i falls exponentially with time by spontaneous emission. The time in which the population falls to $1/e$ of its initial value at $t = 0$ is called the *natural or radiative lifetime* τ_i of level i, where $\tau_i = 1/A_i$. The magnitude of this lifetime is determined by the actual probabilities of transitions from level i by spontaneous emission.

Transitions which are likely to occur are called allowed transitions, those which are unlikely are said to be forbidden. Allowed transitions in the visible spectral range have A_{ij} coefficients in the range of above $10^6\, s^{-1}$, whereas forbidden transitions in this spectral range have A_{ij} coefficients below $10^4\, s^{-1}$. These probabilites decrease as the wavelength of the transition increases. It turns out that there are no transitions to be absolutely forbidden, but some transitions are so unlikely that populated levels are very long lived. They are said to be metastable. Levels with lifetimes in excess of one hour have been observed under laboratory conditions.

Real transitions are not infinitely sharp, they are smeared out or broadened. A particle in a given energy level can have any energy within a finite range. The frequency spectrum of the spontaneous emitted radiation is described by the *lineshape function*, $g(\nu)$. This function is usually normalized for a single transition so that

$$\int_0^\infty g(\nu)d\nu = 1 \quad \Rightarrow \quad \int_{-\infty}^\infty g(\nu)d\nu = 1 \tag{1.48}$$

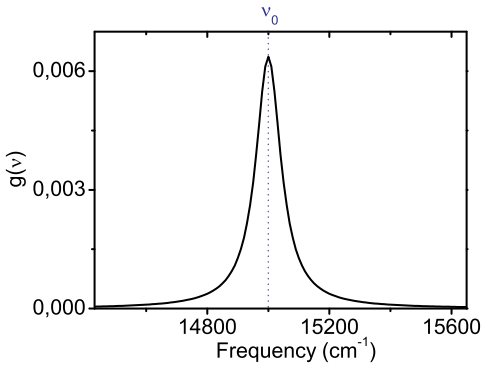


Abbildung 1.7. Lorentzian line shape with central frequency ν_0.

$g(\nu)d\nu$ represents the spectral density of photons emitted spontaneously in the frequency range $\nu + d\nu$. The lineshape function $g(\nu)$ is usually sharply peaked near some frequency ν_0, as shown in Fig.(1.2.1), and is frequently written $g(\nu_0, \nu)$ to highlight this. The integration limits ranging from $-\infty$ to ∞ because then $g(\nu)$ can be viewed as the Fourier transform of a real function of time. For a plane wave we introduce the concept of *intensity*, I, with units $W\,m^{-2}$. The intensity is the average amount of energy per second transported across the unit area in the direction of the wave. The spectral distribution of the intensity, $I(\nu)$, is related to the total intensity, I_0, by

$$I(\nu) = I_0 g(\nu) \tag{1.49}$$

Note, that real plane waves do not exist. Similarly, the spectral distribution of the power, $W(\nu)$, is related to the total power, W_0 by

$$W(\nu) = W_0 g(\nu) \tag{1.50}$$

For a collection of identical particles with the population density N_i the total spontaneously emitted power per frequency interval is

$$W(\nu) = N_i A_i h\nu g(\nu) \tag{1.51}$$

and is decreasing with time if the population density decreases.

1.2.2 Stimulated Emission

In addition to spontaneous emission, transitions can be stimulated by the action of an external radiation field, as shown in Fig. (1.2.2). Let the energy density of the externally applied radiation field at frequency ν be $p(\nu)$ and $[p(\nu)] = Jsm^{-3}$. The rate at which stimulated emission occurs is $N_2 B'_{21}(\nu)$ where B'_{21} is a function specific to the transition between the two level $2 \rightarrow 1$ and its frequency

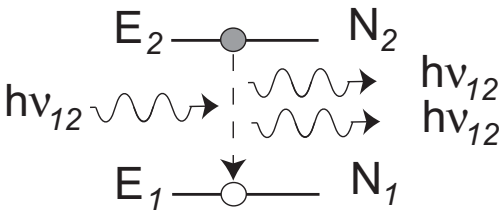


Abbildung 1.8. Process of stimulated emission in a two level system.

dependence is the same as the lineshape function

$$B'_{21}(\nu) = B_{21} g(\nu_0, \nu). \tag{1.52}$$

B_{21} is called the *Einstein coefficient* for stimulated emission. The total rate of change of population density by stimulated emission is

$$\frac{dN_2}{dt} = -N_2 \int_{-\infty}^{\infty} B'_{21} p(\nu) d\nu \tag{1.53}$$

$$= -N_2 B_{21} \int_{-\infty}^{\infty} g(\nu_0, \nu) p(\nu) d\nu \tag{1.54}$$

with units of $[B_{21}] = m^3 J^{-1} s^{-2}$. The energy of a radiation field $p(\nu)$ is related to the intensity $I(\nu)$ by

$$p(\nu) = \frac{I(\nu)}{c}. \tag{1.55}$$

and the number of photons at given intensity is

$$N_{photons} = \frac{I(\nu)}{h\nu}. \tag{1.56}$$

The ideal monochromatic radiation field at frequency ν_{21} has an infinitely narrow energy density profile at ν_{21} and the differential equation in (1.54) is then

$$\frac{dN_2}{dt} = -N_2 B_{21} \int_{-\infty}^{\infty} g(\nu_0, \nu) p_{21} \delta(\nu - \nu_{21}) d\nu = -N_2 B_{21} p_{21} g(\nu_0, \nu_{21}) \tag{1.57}$$

Note, the rate of stimulated emissions produced by the input monochromatic radiation is directly proportional to the value of the lineshape function at the input frequency. If the stimulating radiation field has a spectrum that is broad, and we can assume the energy density $p(\nu) = p(\nu_0)$ as constant where $g(\nu_0, \nu)$ is significant, the differential equation becomes

$$\frac{dN_2}{dt} = -N_2 B_{21} \int_{-\infty}^{\infty} g(\nu_0, \nu) p(\nu_0) d\nu = -N_2 B_{21} p(\nu). \tag{1.58}$$

1.2.3 Stimulated Absorption

As well as stimulating transitions in a downward direction ($2 \rightarrow 1$), transitions can be stimulated from a lower to a higher level ($1 \rightarrow 2$). The rate of such absorptions is

$$N_1 p(\nu) B_{12} g(\nu_0, \nu) \tag{1.59}$$

which gives a result similar to Eq. (1.54)

$$\frac{dN_1}{dt} = -N_1 B_{12} \int_{-\infty}^{\infty} g(\nu_0, \nu) p(\nu) d\nu. \tag{1.60}$$

B_{12} is a constant specific to the transition and is called the Einstein coefficient for stimulated absorption, with $p(\nu)$ the energy density of the stimulating radiation field. There is no analog in the absorption process to spontaneous emission, since a particle cannot spontaneously gain energy without an external energy supply. In stimulated emission the emitted photon has exactly the same frequency as the stimulating photon. In absorption the incident photon disappears, as shown in Fig. (1.2.3). In both processes the particle (atom, molecule, ion, etc.) recoils to conserve linear momentum.

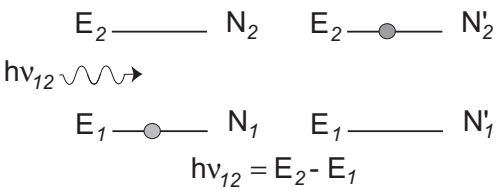


Abbildung 1.9. Stimulated absorption in a two level system. The photon absorbed after the interaction.

1.3 Relation between Einstein coefficients

In thermal equilibrium the populations of the two levels in our two level system N_1 and N_2 are constant

$$\frac{dN_2}{dt} = \frac{dN_1}{dt} = \frac{d(N_1 + N_2)}{dt} = 0 \tag{1.61}$$

and the rates of the transitions between the levels are equal. Since the energy density of the black-body radiation field is nearly constant over the range of the lineshape function where the transitions between level 2 and 1 takes place, we calculate the differential equations in thermal equilibrium with (1.44), (1.54) and

(1.60) to be

$$\frac{dN_2}{dt} = -N_2 B_{21} p(\nu) - A_{21} N_2 + N_1 B_{12} p(\nu) \tag{1.62}$$

$$\frac{dN_1}{dt} = -N_1 B_{12} p(\nu) + A_{21} N_2 + N_2 B_{21} p(\nu) \tag{1.63}$$

$$\Rightarrow \quad \frac{N_2}{N_1} = \frac{B_{12} p(\nu)}{B_{21} p(\nu) + A_{21}} \tag{1.64}$$

The ratio of the population densities of two levels with energy difference $h\nu$ is

$$\frac{N_2}{N_1} = e^{-h\nu/k_B T} \tag{1.65}$$

$$\Rightarrow \quad e^{-h\nu/k_B T} = \frac{B_{12} p(\nu)}{B_{21} p(\nu) + A_{21}} \tag{1.66}$$

$$\Rightarrow \quad p(\nu)(B_{21} e^{-h\nu/k_B T} - B_{12}) = -A_{21} e^{-h\nu/k_B T} \tag{1.67}$$

$$\Rightarrow \quad p(\nu) = \frac{A_{21}}{B_{12} e^{h\nu/k_B T} - B_{21}} \tag{1.68}$$

$$\Rightarrow \quad \frac{8\pi h\nu^3}{c^3 (e^{h\nu/k_B T} - 1)} = \frac{A_{21}}{B_{12} e^{h\nu/k_B T} - B_{21}} \tag{1.69}$$

The last equality can only be satisfied if

$$B_{12} = B_{21} \tag{1.70}$$

and

$$A_{21} = B_{21} \frac{8\pi h\nu^3}{c^3}. \tag{1.71}$$

Equations (1.70) and (1.71) are called *Einstein relations*. The spontaneous emission rate, A_{21}, is independent of external radiation field and is important for the energy density $p(\nu)$, because with $A_{21} = 0$ it follows from (1.68)that $p(\nu) \equiv 0$. Note, that contributions of the spontaneous emission increase with ν^3 with respect to contributions of stimulated emission. This is very important for the development of lasers where a population inversion between two levels induce a strong stimulated emission signal (LASER: Light amplification by stimulated emission of radiation).

1.3.1 Level Degeneracy

In real systems it frequently happens that a given energy level corresponds to a number g of different arrangements, where g is the *degeneracy* of the level. The separate states of the system with the same energy are called sub-levels. Assume the levels 2 and 1 consist of a number of sub-levels g_2 and g_1. For each of the sub-levels of level 1 and 2 with populations n_1 and n_2 the ratio of populations is

$$\frac{n_2}{n_1} = e^{-h\nu/k_B T} \tag{1.72}$$

and $N_1 = g_1 n_1$, $N_2 = g_2 n_2$. Therefore

$$\frac{n_2}{n_1} = \frac{g_1 N_2}{g_2 N_1} \tag{1.73}$$

and

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-h\nu/k_B T} \tag{1.74}$$

and from (1.64) it gives

$$\frac{N_2}{N_1} = \frac{B_{12}p(\nu)}{B_{21}p(\nu) + A_{21}} = \frac{g_2}{g_1} e^{-h\nu/k_B T} \tag{1.75}$$

$$\Rightarrow \quad p(\nu)[g_2 B_{21} e^{-h\nu/k_B T} - g_1 B_{12}] = -A_{21} g_2 e^{-h\nu/k_B T} \tag{1.76}$$

$$\Rightarrow \quad p(\nu) = \frac{g_2 A_{21}}{g_1 B_{12} e^{h\nu/k_B T} - g_2 B_{21}} \tag{1.77}$$

$$\Rightarrow \quad \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1} = \frac{A_{21}}{\frac{g_1}{g_2} B_{12} e^{h\nu/k_B T} - B_{21}} \tag{1.78}$$

$$\Rightarrow \quad \frac{g_1}{g_2} B_{12} = B_{21} \tag{1.79}$$

and

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}. \tag{1.80}$$

It is instructive to examine the relative rates at which spontaneous and stimulated processes occur in a system at temperature T. The ratio is

$$R = \frac{A_{21}}{B_{21}p(\nu)} = e^{h\nu/k_B T} - 1 = \frac{1}{\overline{n}(\nu)}. \tag{1.81}$$

Here, $p(\nu)$ is the black-body radiation field and the average number of photons in a mode in the case of black-body radiation is

$$\overline{n}(\nu) = \frac{1}{e^{h\nu/k_B T} - 1}. \tag{1.82}$$

For T=300 K and $\lambda = 500\,nm$ or $\nu = 6 \times 10^{14}\,s^{-1}$ the ratio $h\nu/k_B T$ is

$$\frac{h\nu}{k_B T} = \frac{6.626 \times 10^{-34}\,Js \times 6 \times 10^{14}\,s^{-1}}{1.38 \times 10^{-23}\,JK^{-1} \times 300\,K} \approx 96. \tag{1.83}$$

and so the ratio, R, of spontaneous and stimulated processes

$$R = e^{96} - 1 \approx 5 \times 10^{41} \quad \Rightarrow \quad \overline{n}(\nu) = 2 \times 10^{-42} \tag{1.84}$$

is very high. In the visible and near-infrared region spontaneous emission is generally dominates unless there are several photons in a mode ($\overline{n}(\nu) > 1$).

In a disperse medium the refractive index varies with frequency. There the mode density $\widehat{p}(\nu)$ of a black-body cavity has to be modified to

$$\widehat{p}(\nu) = \frac{8\pi\nu^2 n^2 n_g}{c_0^3} \tag{1.85}$$

with

$$n_g = n + \nu\frac{dn}{d\nu}. \tag{1.86}$$

The ratio of A_{21}/B_{21} changes without changing the ratio of spontaneous and stimulated processes.

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3 n^2 n_g}{c_0^3}. \tag{1.87}$$

1.4 Fouriertransformation

In a multitude of physical and mathematical problems it is necessary to develop a periodic function $f(t)$ with period of 2π by a sum of trigonometric functions.

$$f(t) = \frac{a_0}{2} + \sum_{k=1}^{\infty}(a_k \cos(kt) + b_k \sin(kt) \tag{1.88}$$

Periodic processes are known from dynamic properties of music and sounds, the movement of planets, a pendulum, etc. The trigonometric functions to describe periodic processes are the sine and cosine functions, which have very nice properties:

$$\begin{aligned}
\sin(\omega t) &= -\sin(-\omega t) && (1.89)\\
\cos(\omega t) &= \cos(-\omega t) && (1.90)\\
\cos(\omega t) &= \sin(\omega t + \frac{\pi}{2}) && (1.91)\\
\sin(\omega_1 t \pm \omega_2 t) &= \sin(\omega_1 t)\cos(\omega_2 t) \pm \cos(\omega_1 t)\sin(\omega_2 t) && (1.92)\\
\cos(\omega_1 t \pm \omega_2 t) &= \cos(\omega_1 t)\cos(\omega_2 t) \mp \sin(\omega_1 t)\sin(\omega_2 t) && (1.93)\\
1 &= \sin^2(\omega_1 t) + \cos^2(\omega_1 t) && (1.94)\\
\sin(2\omega_1 t) &= 2\sin(\omega_1 t)\cos(\omega_1 t) && (1.95)\\
\cos(2\omega_1 t) &= \cos^2(\omega_1 t) - \sin^2(\omega_1 t) && (1.96)\\
\sin^2(\omega_1 t) &= \frac{1}{2}(1 - \cos(2\omega_1 t)) && (1.97)\\
\sin(\frac{\omega_1 t}{2}) &= \pm\sqrt{\frac{1-\cos(\omega_1 t)}{2}} && (1.98)\\
\cos(\frac{\omega_1 t}{2}) &= \pm\sqrt{\frac{1+\cos(\omega_1 t)}{2}} && (1.99)\\
\sin(\omega_1 t) + \sin(\omega_2 t) &= 2\sin(\frac{\omega_1 t + \omega_2 t}{2})\cos(\frac{\omega_1 t - \omega_2 t}{2}) && (1.100)
\end{aligned}$$

and properties of the derivatives:

$$\begin{aligned}
\frac{d}{dt}\sin(\omega_1 t) &= \omega_1 \cos(\omega_1 t) && (1.101)\\
\frac{d}{dt}\cos(\omega_1 t) &= -\omega_1 \sin(\omega_1 t) && (1.102)\\
\overrightarrow{\bigtriangledown}\sin(\overrightarrow{k}\cdot\overrightarrow{x}) &= \overrightarrow{k}\cos(\overrightarrow{k}\cdot\overrightarrow{x}) && (1.103)\\
e^{i\omega_1 t} &= \cos(\omega_1 t) + i\sin(\omega_1 t) && (1.104)\\
\cos(\omega_1 t) &= \frac{1}{2}\left[e^{i\omega_1 t} + e^{-i\omega_1 t}\right] && (1.105)\\
\sin(\omega_1 t) &= \frac{1}{2i}\left[e^{i\omega_1 t} - e^{-i\omega_1 t}\right] && (1.106)\\
\int \cos^2(\omega_1 t)dt &= \frac{1}{2}t + \frac{1}{4\omega_1}\sin(2\omega_1 t). && (1.107)
\end{aligned}$$

In Hilbert space ($\mathfrak{L}^2$) with period 2π the functions $\left\{\frac{1}{\sqrt{2\pi}}, \frac{1}{\sqrt{\pi}}\sin(\omega_1 t), \frac{1}{\sqrt{\pi}}\cos(\omega_1 t), \frac{1}{\sqrt{\pi}}\sin(2\omega_1 t), \frac{1}{\sqrt{\pi}}\cos(2\omega_1 t), \ldots\right\}$ are eigenvectors and span the whole Hilbert space. They form an orthogonal and normalized basis, since

$$\frac{1}{T}\int_{-T}^{T}\sin(\omega_1 t)\sin(\omega_2 t)dt = \delta(\omega_1 - \omega_2). \tag{1.108}$$

For every periodic function $g(t)$, which is a member of $\mathfrak{L}^2$ with period 2π, the deviation between $g(t)$ and the trigonometric representation $f_n(t)$ becomes

$$\lim_{n\to\infty}\int_{-\pi}^{\pi}(g(t) - f_n(t))^2 dt = 0 \tag{1.109}$$

Equation (1.109) describes the convergence in the quadratic average. The Fourier sum $\sum_n f_n(t)$ converges only for every single point $\lim_{n\to\infty} f_n(t) = f(t)$ if the function $g(t)$ is continous. If the function $g(t)$ has points of discontinouity at t_u, then the Fourier sum becomes at t_u (Dirichlet):

$$f(t_u) = \lim_{h\to 0}\frac{g(t_u + h) + g(t_u - h)}{2} \tag{1.110}$$

An example for this is plotted in Fig. 1.4h. If every periodic continous function can be expressed by the Fourier sum, the question is how to get the Fourier coefficients a_k and b_k. In Fig. 1.4 we tried to guess the Fourier coefficients. To

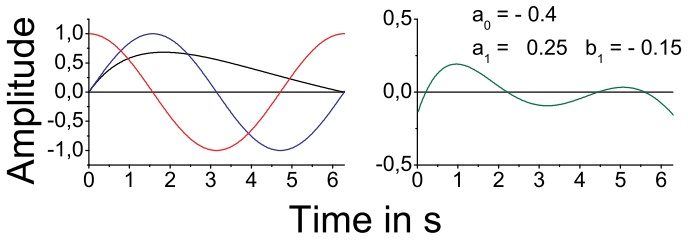


Abbildung 1.10. First steps of representing an arbitrary periodic function (black), as a sum of trigonometric functions.

calculate the Fourier coefficients we can make use of the orthogonality relation. We take the function $g(t)$ multiply it with the individual eigenfunctions, and

integrate over the period:

$$a_k = \frac{1}{\pi}\int_{-\pi}^{\pi} g(t)\cos(kt)dt, \quad \mathrm{k} = 0, 1, 2, \ldots \tag{1.111}$$

$$b_k = \frac{1}{\pi}\int_{-\pi}^{\pi} g(t)\sin(kt)dt, \quad \mathrm{k} = 1, 2, \ldots \tag{1.112}$$

This is nothing else than projecting out the contribution of the eigenfunction analog to $(a, b, c) \bullet \mathbf{e_x} = a$.

The Fourier coefficients of periodic function over the interval $(-T, \ldots, T)$ is given by

$$a_k = \frac{1}{T}\int_{-T}^{T} g(t')\cos(\frac{k\pi t'}{T})dt', \quad \mathrm{k} = 0, 1, 2, \ldots \tag{1.113}$$

$$b_k = \frac{1}{T}\int_{-T}^{T} g(t')\sin(\frac{k\pi t'}{T})dt', \quad \mathrm{k} = 1, 2, \ldots \tag{1.114}$$

Summing up the contributions of the Fourier coefficients gives smooth functions with negligible oscillatory features (Fig. 1.4). Note, if the Fourier coefficients are a_k and b_k, the phase φ_k is given by:

$$A_k^2 = a_k^2 + b_k^2 \tag{1.115}$$

$$a_k = A_k \cos\varphi_k \tag{1.116}$$

$$b_k = A_k \sin\varphi_k \tag{1.117}$$

$$\varphi_k = \tan\left(\frac{b_k}{a_k}\right) \tag{1.118}$$

Note, the Fourier sum can be written as

$$f(t) = a_0 + \sum_k A_k \cos\varphi_k \cos(\frac{2\pi}{T}kt) + A_k \sin\varphi_k \sin(\frac{2\pi}{T}kt) \tag{1.119}$$

$$= a_0 + \sum_k A_k \cos(\frac{2\pi}{T}kt - \varphi_k) \tag{1.120}$$

Fourier sums can be expanded to nonperiodic functions if the following relation holds:

$$\int_{-\infty}^{\infty} |g(t)|dt < \infty. \tag{1.121}$$

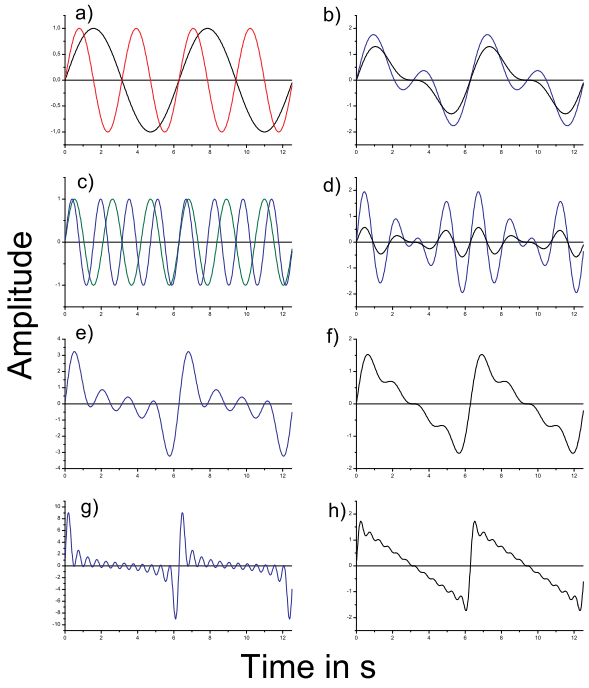


Abbildung 1.11. a) Sine functions with frequencies 1 (black) and 2 (red); b) sum of sine functions of a) (blue) and weighted sum of sine functions of a) with $\sum_k \frac{1}{k}\sin(kt)$ (black); c) Sine functions with frequencies 3 and 4; d) sum of functions in c) and weighted sum of functions in c); e) sum of functions with frequencies 1 to 4; f) weighted sum of functions with frequencies 1 to 4; g) same as e) but with 12 frequencies $\sum_{k=1}^{12}\sin(kt)$; h) $\sum_{k=1}^{12}\frac{1}{k}\sin(kt)$.

This means, that the function becomes zero for $t \to \infty$ and $t \to -\infty$. These points are the analogue points to the points at $-T$ and T for periodic functions. The continous Fourier transformation $\widehat{f}(t)$ of $f(t)$ is given by:

$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \widehat{f}(\omega) e^{-i\omega t} d\omega \tag{1.122}$$

$$\widehat{f}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{i\omega t} dt \tag{1.123}$$

The Fourier transformation $\widehat{f}(\omega)$ is given by the Cosine Fourier transformation

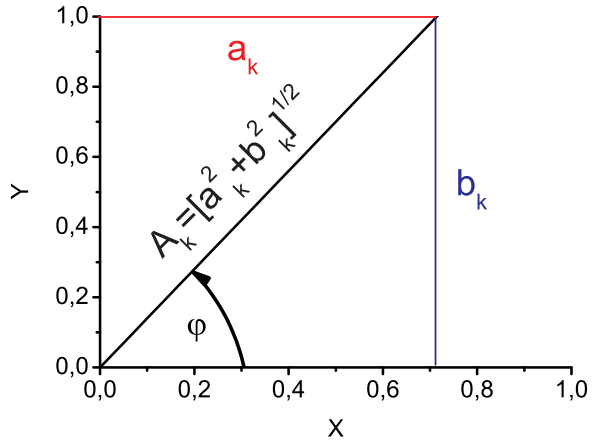


Abbildung 1.12. Representation of the phase φ.

and the Sine Fourier transformation:

$$f_c(t) = \sqrt{\frac{2}{\pi}} \int_0^\infty \widehat{f}_c(\omega) \cos(\omega t) d\omega \tag{1.124}$$

$$\widehat{f}_c(\omega) = \sqrt{\frac{2}{\pi}} \int_0^\infty f_c(t) \cos(\omega t) dt \tag{1.125}$$

$$f_s(t) = \sqrt{\frac{2}{\pi}} \int_0^\infty \widehat{f}_s(\omega) \sin(\omega t) d\omega \tag{1.126}$$

$$\widehat{f}_s(\omega) = \sqrt{\frac{2}{\pi}} \int_0^\infty f_s(t) \sin(\omega t) dt \tag{1.127}$$

$$\tag{1.128}$$

For an even function f(t) the Fourier transformation is given by $\widehat{f}(t) = \widehat{f}_c(t)$, for an odd function the Fourier transformation is given by $\widehat{f}(t) = i\widehat{f}_s(t)$. Every function $f(t)$ can be written as a sum of an even and an odd function:

$$f(t) = g(t) + h(t) \tag{1.129}$$

$$g(t) = \frac{1}{2}[f(t) + f(-t)] \tag{1.130}$$

$$h(t) = \frac{1}{2}[f(t) - f(-t)] \tag{1.131}$$

$$\widehat{f}(\omega) = \widehat{g}_c(\omega) + i\widehat{h}_s(\omega) \tag{1.132}$$

Therefore, we can concentrate on the Cosine and Sine Fourier transformation.

The Fourier transformation has additional importance for the folding technique of functions:

$$\mathfrak{C}_{fg}(t) = \int_{-\infty}^{\infty} f(\tau)g(t-\tau)d\tau = (f \star g)(t) \tag{1.133}$$

$$\widehat{f}(\omega)\widehat{g}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}(f \star g)(t)e^{i\omega t}dt \tag{1.134}$$

Some examples of Fourier transformations are:

$$f(t) = e^{-at^2} \Rightarrow \widehat{f}(\omega) = \frac{1}{\sqrt{2}}\, a^{-\frac{1}{2}} e^{-\frac{\omega^2}{4a}} \tag{1.135}$$

$$f(t) = e^{-at} \Rightarrow \widehat{f}(\omega) = \sqrt{\frac{2}{\pi}}\frac{a}{a^2+\omega^2} \tag{1.136}$$

$$f(t) = \left\{ \begin{array}{lcl} 1 & , & |t| < a \\ 0 & , & else \end{array} \right\} \Rightarrow \widehat{f}(\omega) = 2\sqrt{\frac{2}{\pi}}\frac{\sin(a\omega)}{\omega} \tag{1.137}$$

Numeric Fourier transformations are presented in the following figures. Note, that the intensity amplitudes in the time domain are given by the power amplitudes $A(\omega)A^*(\omega)$ of the Fourier transformation. Information on the timing of processes are reflected in the phase, given by the real and imaginary part of the amplitudes. Short processes in time result in broad features in frequency and vice versa.

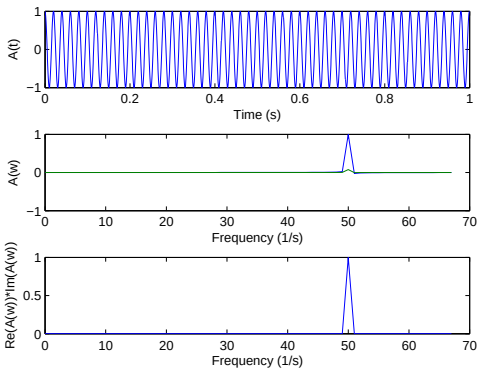


Abbildung 1.13. Cosine function with frequency of 50 Hz and amplitude 1.

A phase shift of $\pi/2$ introduce a sign change in the imaginary amplitude and a vanishing of the real amplitude (Fig. 1.4)

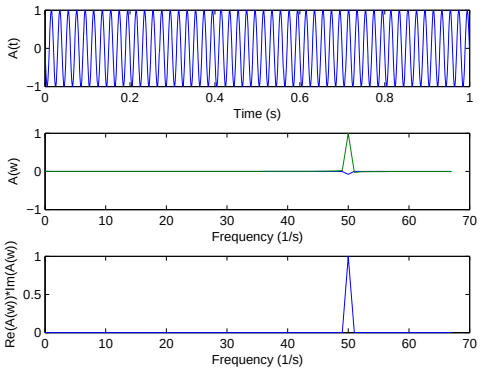


Abbildung 1.14. Cosine function with frequency of 50 Hz, amplitude 1 and phase $\pi/2$.

For a beating you need at least two frequencies (Fig. 1.4).

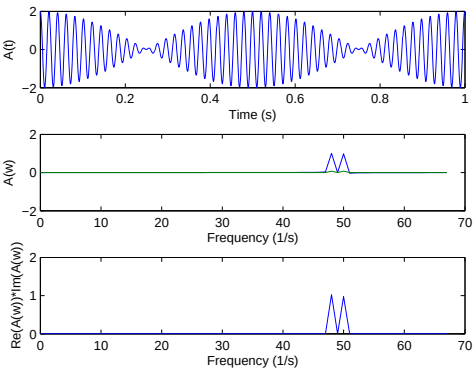


Abbildung 1.15. Cosine functions with frequencies of 48 and 50 Hz and amplitudes of 1 and 1, respectively.

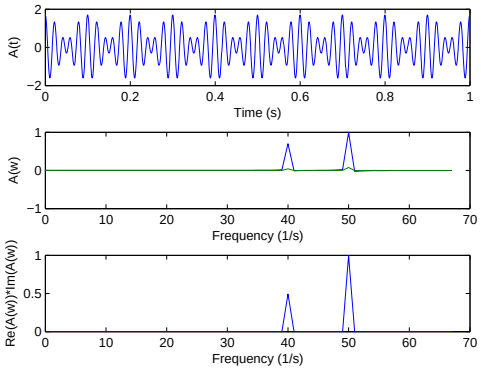


Abbildung 1.16. Cosine functions with frequencies of 40 and 50 Hz and amplitudes of 0.7 and 1, respectively.

A phase shift of π introduce a sign change in the real amplitude and a change in the imaginary amplitude (Fig. 1.4).

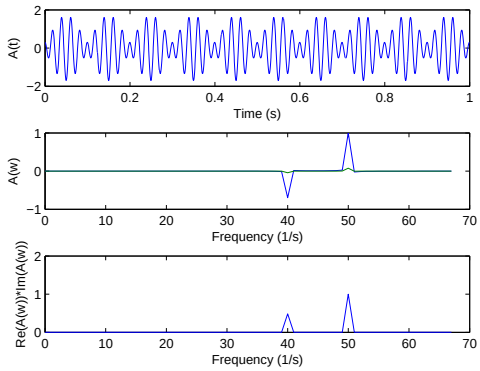


Abbildung 1.17. Cosine functions with frequencies of 40 and 50 Hz and amplitudes of 0.7 and 1, respectively. The 40 Hz Cosine oscillation is phase shifted by π.

A phase shift of $\pi/2$ introduce a strong change in the imaginary amplitude and a vanishing in the real amplitude (Fig. 1.4).

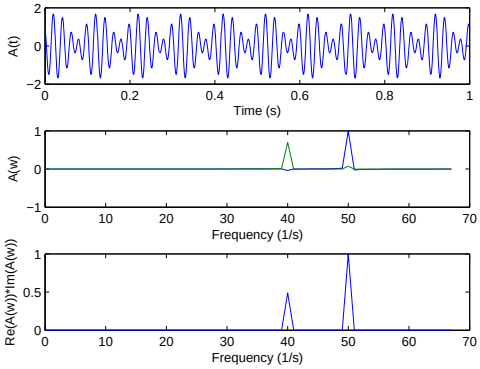


Abbildung 1.18. Cosine functions with frequencies of 40 and 50 Hz and amplitudes of 0.7 and 1, respectively. The 40 Hz Cosine oscillation is phase shifted by $\pi/2$.

If the frequencies are multiples of each other the information of the amplitude can be represented by the imaginary amplitude and the real amplitude of the multiple frequency. Note, a quarter of the higher frequency is the lower one, and a quarter of 2π is $\pi/2$ (Fig. 1.4). A phase shift of $\pi/2$ reverses again the real and

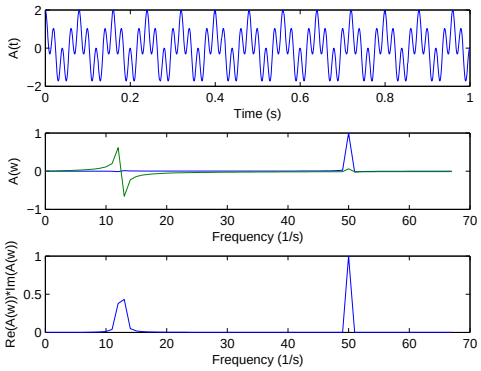


Abbildung 1.19. Cosine functions with frequencies of 12.5 and 50 Hz and amplitudes of 1 and 1, respectively.

imaginary part of the 12.5 Hz amplitudes (Fig. 1.4).

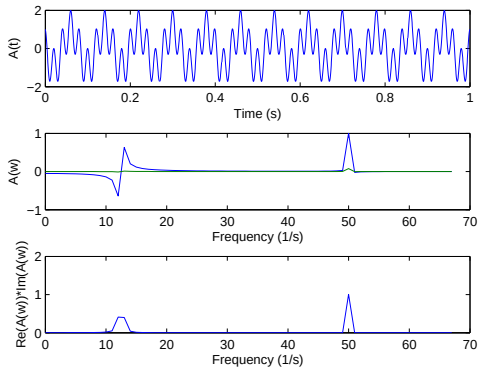


Abbildung 1.20. Cosine functions with frequencies of 12.5 and 50 Hz and amplitudes of 1 and 1, respectively. The 12.5 Hz Cosine oscillation is phase shifted by $\pi/2$.

An exponential rise and decay time of an oscillatory signal induce frequency broadening of the 50 Hz carrier frequency (Fig. 1.4).

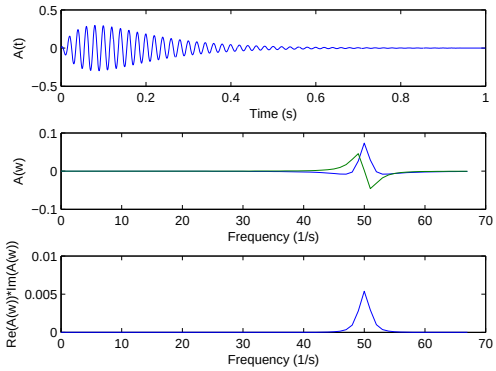


Abbildung 1.21. Carrier frequency of 50 Hz with an exponential rise time of 0.1 s and a decay time of 0.13 s.

The timing of where the Gaussian envelope function has its maximum is given by the imaginary amplitude (Fig. 1.4).

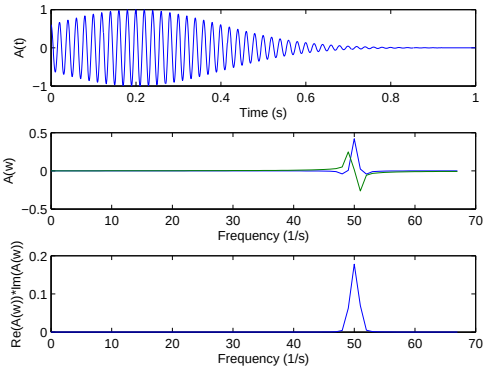


Abbildung 1.22. One Gaussian envelope function with a width of $\sigma = 0.2$ and carrier frequency of 50 Hz, centered around 0.7 s.

The imaginary amplitude changes if the timing changes (Fig. 1.4).

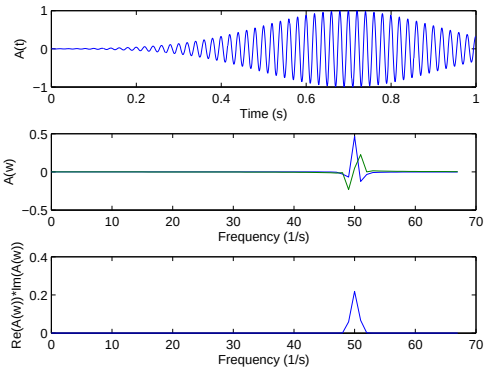


Abbildung 1.23. One Gaussian envelope function with a width of $\sigma = 0.2$ and carrier frequency of 50 Hz, centered around 0.2 s.

The sum of both differently timed Gaussian functions gives the sum of all contribution, including the imaginary part (Fig. 1.4). It is not trivial to see by the

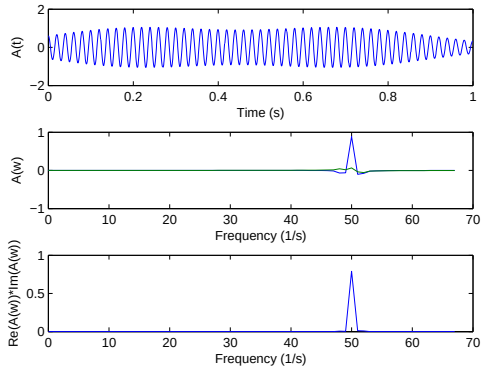


Abbildung 1.24. Sum of two Gaussian envelope functions centered around 0.2 s and 0.7 s; widths of $\sigma = 0.2$ and carrier frequency of 50 Hz.

real and imaginary part how the timing looks like. On top of that in real Fourier transformations, which are limited in accuracy, there is a big problem for long time signals. If for example, in a symphony a single frequency is played all the time and it should be off for only one second after 20 minutes, this affords enormous accuracy. Here, small phase shifts would not reduce but increase the single frequency, so that other ways of storing, analyzing, and compressing are used. Wavelet transformations are very useful for such problems. They form the basis sets for JPG and PNG formats.

Folding integrals are important in spectroscopy. They describe the signals mea-

sured in experiments. For example an exponential function g(t) is folded with the system response function of the experimental set up r(t) (Fig. 1.4). The measured signal S(t) is defined by the convolution function:

$$S(t) = \int_{-\infty}^{\infty} g(\tau) r(t-\tau) d\tau \tag{1.138}$$

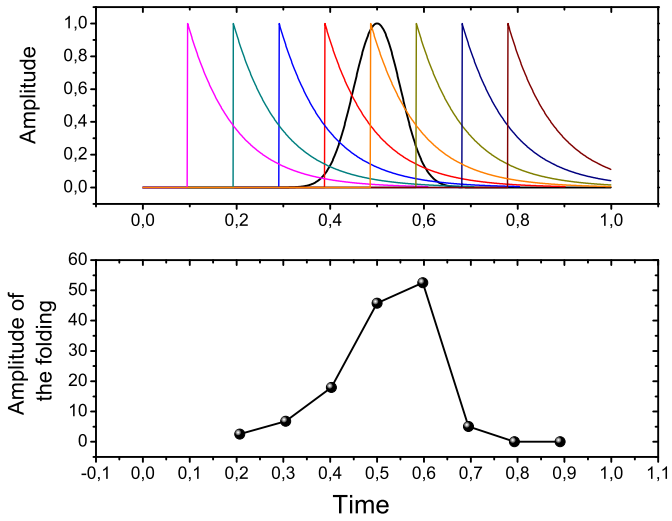


Abbildung 1.25. Upper panel: Exponentials g(t) and a Gaussian function (black) r(t) for different displacement times t_i. Lower panel: Folding function $S(t)$ of the Gaussian with an exponential. For each displacement in time t_i between the exponential and Gaussian function, the integral over the product is calculated and gives rise to $S(t_i)$. Note, the time scale is reversed and goes from rihght to left.

1.5 Homogeneous Line Broadening

As shown before the lifetimes of an excited state is given by the natural lifetime $\tau_i = 1/A_i$. If we consider many particles with the same lifetime excited simultaneously with a coherent light source, they would emit an electric field of the decaying excited particles (for $t \geq 0$) as

$$E(t) = E_0 e^{-t/\tau_c} cos\omega_0 t. \tag{1.139}$$

In the case of incoherent excitation the electric field of a single atom is given by

$$E(t) = E_0 e^{-t/\tau_c} cos(\omega_0 t + \varphi). \tag{1.140}$$

The time constant τ_c describes the damping of the electric field. The intensity $I(t)$ emitted by an individual excited particle is

$$I(t) \propto |E(t)|^2 = E_0^2 e^{-2t/\tau_c} cos^2(\omega_0 t). \tag{1.141}$$

For many such particles the total observed intensity is

$$\begin{aligned} I(t) = \sum_k I_k(t) &\propto \sum_k E_0^2 e^{-2t/\tau_c} cos^2(\omega_0 t + \varphi_k) && (1.142)\\ &= \sum_k \frac{E_0^2}{2} e^{-2t/\tau_c}[1 + cos2(\omega_0 t + \varphi_k)] && (1.143)\\ &= k\frac{E_0^2}{2} e^{-2t/\tau_c} \quad = k \quad \frac{E_0^2}{2} e^{-t/\tau_i} && (1.144) \end{aligned}$$

We see that the lifetime τ_i is two times faster than the dephasing time $\tau_c = 2\tau_i$. This is because the dephasing time is related to the electric field amplitude and the lifetime to the electric field intensity. The electric field is now (for $t \geq 0$)

$$\begin{aligned} E(t) &= E_0 e^{-t/2\tau_i} cos(\omega_0 t) = \frac{E_0}{2} e^{-t/2\tau_i}[e^{i\omega_0 t} + e^{-i\omega_0 t}] && (1.145)\\ &= \frac{E_0}{2}[e^{i(\omega_0 + i/2\tau_i)t} + e^{-i(\omega_0 - i/2\tau_i)t}] && (1.146) \end{aligned}$$

The frequency distribution of the signal is given by its Fourier transform $E(\omega)$:

$$E(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} E(t)e^{-i\omega t}dt \quad (1.147)$$

$$= \frac{1}{\pi}\int_{0}^{\infty} \frac{E_0}{2}[e^{i(\omega_0+i/2\tau_i)t} + e^{-i(\omega_0-i/2\tau_i)t}]e^{-i\omega t}dt \quad (1.148)$$

$$= \frac{E_0}{2\pi}\int_{0}^{\infty} [e^{i(\omega_0-\omega+i/2\tau_i)t} + e^{-i(\omega_0+\omega-i/2\tau_i)t}]dt \quad (1.149)$$

$$= \frac{E_0}{2\pi}[\frac{1}{i(\omega_0-\omega+i/2\tau_i)}(0-1) + \frac{1}{-i(\omega_0+\omega-i/2\tau_i)}(0-1)] \quad (1.150)$$

$$= \frac{E_0}{2\pi}[\frac{i}{(\omega_0-\omega+i/2\tau_i)} - \frac{i}{(\omega_0+\omega-i/2\tau_i)}] \quad (1.151)$$

$$= \frac{E_0}{2\pi}[\frac{i}{(\omega_0-\omega+i/2\tau_i)}] \quad (1.152)$$

Only frequencies with $\omega \geq 0$ are physical. The intensity of emitted radiation is then given by

$$I(\omega) \propto |E(\omega)|^2 = E(\omega)E^*(\omega) \quad (1.153)$$

$$I(\omega) \propto \frac{E_0^2}{4\pi^2}[\frac{i(\omega_0-\omega)+1/2\tau_i}{(\omega_0-\omega)^2+(1/2\tau_i)^2} \times \frac{-i(\omega_0-\omega)+1/2\tau_i}{(\omega_0-\omega)^2+(1/2\tau_i)^2}] \quad (1.154)$$

$$\propto \frac{E_0^2}{4\pi^2} \times \frac{1}{(\omega_0-\omega)^2+(1/2\tau_i)^2} \quad (1.155)$$

$$I(\nu) \propto \frac{E_0^2}{4\pi^2} \times \frac{1}{(\nu_0-\nu)^2+(1/4\pi\tau_i)^2} \quad (1.156)$$

This type of function is called a Lorentzian. Since natural broadening is the same

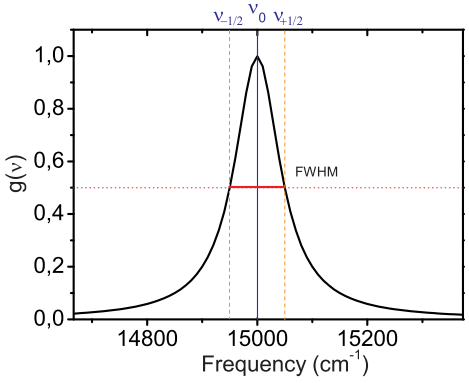


Abbildung 1.26. Lorentzian line shape with FWHM at $\Delta\nu = \frac{1}{2\pi\tau_i}$.

for each particle, this broadening mechanism is called *homogeneous* broadening.

The full width at half maximum height (FWHM) of this function is found from half intensity points of $I(\nu)$ that occur at frequencies $\nu_{\pm\frac{1}{2}}$ as shown in Fig. (1.5), where

$$(\frac{1}{4\pi\tau_i})^2 = (\nu_{\pm\frac{1}{2}} - \nu_0)^2. \tag{1.157}$$

The FWHM is given by

$$\Delta\nu = \frac{1}{2\pi\tau_i} = \frac{\sum_j A_{ij}}{2\pi} \quad \text{with} \quad \Delta\nu = \nu_{+\frac{1}{2}} - \nu_{-\frac{1}{2}} \tag{1.158}$$

The normalized form of the Lorentzian lineshape function for natural broadening (Fig. 1.5) is given by

$$g(\nu)_{LN} = \frac{(2/\pi\Delta\nu)}{1 + [2(\nu - \nu_0)/\Delta\nu]^2}. \tag{1.159}$$

Other mechanisms of homogeneous broadening are for example:

- Soft collisions of phonons with the crystal particles, which does not abruptly terminate the lifetime
- Pressure broadening in gaseous and liquid phase by soft collisions with neutral or charged particles
- Stark broadening by a varying external field perturbing the energy levels of the particle
- Resonance interactions reducing the lifetime by energy exchange with neighboring particles.

The effects mention above induce phase shifts resulting in a destruction of the macroscopic coherence of the ensemble, without reducing the population density of the involved levels. If $X_{ij} = 1/\tau_2^*$ is the rate per particle per unit volume by which collisions disturb the macroscopic coherence of the ensemble of level i and $A_{ij} = 1/\tau_i$ is the intensity rate per particle per unit volume for spontaneous emission to state j, we can deduce the decoherence rate τ_c or dephasing time τ_2 by

$$\frac{1}{\tau_c} = \frac{1}{\tau_2} = \sum_j (\frac{1}{2}A_{ij} + X_{ij}) = \frac{1}{2\tau_i} + \frac{1}{\tau_2^*}. \tag{1.160}$$

The rate τ_2^* is called the pure dephasing time.

When the environment or properties of particles in an emitting sample are not

identical, *inhomogeneous* broadening occurs. The normalized lineshape function of an inhomogeneous broadened transition is given by

$$g(\nu)_{GN} = \frac{2}{\Delta\nu}\sqrt{\frac{ln\,2}{\pi}} \times e^{-ln\,2\times[2(\nu-\nu_0)/\Delta\nu]^2} \tag{1.161}$$

This is a Gaussian function with FWHM of $\Delta\nu$. In a gaseous phase an inhomogeneous broadening mechanism is the Doppler broadening. In the condensed phase different interactions to the environment in the non-emitting ground state and the emitting state can lead to inhomogeneous broadening.

Generally in spectroscopic experiments, the investigator disturbs the material system with an external perturbation (force), such as exciting a particle into an emitting state. How long a given property of the system persists until it is averaged out by the microscopic motion of the particles in the system is qualitatively described by a time-correlation function. The time-correlation function $\mathfrak{C}_{AB}(t,t')$ is the product of the pair of dynamic variables $A(t)$ and $B(t')$ averaged over an equilibrium canonical ensemble:

$$\mathfrak{C}_{AB}(t,t') = \langle A(t)B(t')\rangle_E \tag{1.162}$$

The autocorrelation function $\mathfrak{C}_A(t)$ of a dynamic variable $A(t)$ is defined by

$$\mathfrak{C}_A(t) = \langle A(t)A(0)\rangle_E \tag{1.163}$$

The time dependence of the dynamic variable $A(t)$ is determined by the perturbations that arise from thermal motion and molecular interactions. These perturbations induce fluctuations of positions and momenta of particles resulting in phase changes of A(t) over time. The time dependence of the dynamic variable $A(t)$ is very complex, because the environment, consisting of a large number of atoms and molecules, fluctuates in a complex fashion. The time dependence of $A(t)$ will generally resemble a stochastic noise pattern generated by the interaction of various degrees of freedom (Fig. 1.5). A simple example of treating a stochastic process is given by the equation

$$\frac{\partial A(t)}{\partial t} = i\Omega(t)A(t) \tag{1.164}$$

where the time dependence of the frequency $\Omega(t)$ consists of an average part $\omega_0 = \langle\Omega(t)\rangle_E$ and a fluctuating part $\delta\Omega(t)$. If

$$\Omega(t) = \omega_0 + \delta\Omega(t) \tag{1.165}$$

then the average of the fluctuations is

$$\langle\delta\Omega(t)\rangle_E = 0. \tag{1.166}$$

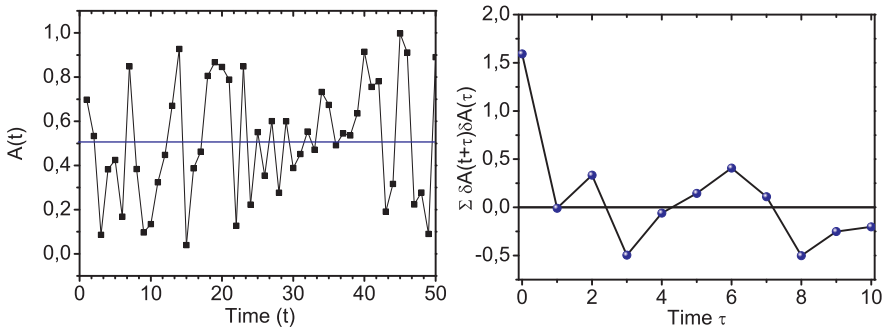


Abbildung 1.27. Random fluctuations in time of the dynamic variable A.

Equations (1.164) and (1.165) define the time dependence of dynamic variable $A(t)$ and $\Omega(t)$ in terms of ω_0 and $\delta\Omega(t)$. The dynamics characterizing $A(t)$ are now incorporated in the random function $\delta\Omega(t)$. If $\delta\Omega(t)$ is known, it is possible to extract dynamic information from $A(t)$ and vice versa. The random variable $\delta\Omega(t)$ is characterized by the variance, defined as

$$\Delta = \sqrt{\langle \delta\Omega^2(0)\rangle_E} = \sqrt{\mathfrak{C}_2(\delta\Omega(0))} \tag{1.167}$$

and by the correlation time τ_c, given by

$$\tau_c = \int_0^\infty \frac{\langle \delta\Omega(t)\delta\Omega(0)\rangle_E}{\langle \delta\Omega(0)\delta\Omega(0)\rangle_E} dt = \frac{1}{\Delta^2}\int_0^\infty \langle \delta\Omega(t)\delta\Omega(0)\rangle_E dt \tag{1.168}$$

The correlation time τ_c is directly related to the random frequency or energy fluctuations of the system and the time-correlation function $\mathfrak{C}_A(t)$ is related to the line-shape function $I_A(\omega)$. Furthermore, Δ is a measure of the coupling strength to the perturbers.

Up to now we focussed on ensemble average time-correlation functions, but in a measurement the dynamic variable $A(t)$ is averaged over an interval of time from t_0 to $t_0 + T$. In an equilibrium system the average is independent of the initial time t_0 at which the measurement started. Thus, the property associated with $A(t)$ can be calculated to

$$\overline{A} = \lim_{T\to\infty} \frac{1}{T}\int_{t_0}^{t_0+T} A(t)dt = \lim_{T\to\infty} \frac{1}{T}\int_0^T A(t)dt. \tag{1.169}$$

Temporal coherence exists if the value of $A(t+\tau)$ is separated from that of $A(t)$ by small values of τ. The coherence is lost, however, if τ is much longer than the correlation or coherence time. A measure of this correlation for the property $A(t)$ separated by a time t is given by the time-averaged time-correlation function, which is defined as

$$\overline{A(t)A(0)} = \overline{A(t)A} = \lim_{T\to\infty} \frac{1}{T}\int_0^T A(t+\tau)A(\tau)d\tau \tag{1.170}$$

In spectroscopic experiments the time-averaged time-correlation function is measured. The ensemble averaged time-correlation function and the time-averaged time correlation function of a single particle are identical for ergodic systems

$$\mathfrak{C}_A(t) = \langle A(t)A(0)\rangle_E = \overline{A(t)A(0)} \equiv \langle A(t)A(0)\rangle_c. \tag{1.171}$$

The time-correlation function (TCF) has the following properties:

$$\langle A^2\rangle_c \geq \langle A(t)A\rangle_c \tag{1.172}$$

$$\lim_{t\to\infty}\langle A(t)A\rangle_c = \langle A\rangle_c^2 \tag{1.173}$$

Equation (1.173) follows because for very long separation times the values of $A(t)$ are no longer correlated, and the average of products becomes the product of averages. That means, the time-correlation function $\mathfrak{C}_A(t)$ decays in time from $\langle A^2\rangle_c$ initially to $\langle A\rangle_c^2$ for large values of time. The details of the time decay depend on the dynamical nature of the physical system. When the average $\langle A\rangle_c$ does not vanish, the fluctuations, δA, in A can be defined by

$$\delta A(t) = A(t) - \langle A(t)\rangle_c \tag{1.174}$$

and the time-correlation function of δA is then given by

$$\langle \delta A(t)\delta A(0)\rangle_c = \langle A(t)A(0)\rangle_c - \langle A\rangle_c^2 \tag{1.175}$$

From this it is evident that the time-correlation function of $\delta A(t)$ always vanishes at long waiting times. The probable range of time where the $\delta A(t)$ values are correlated can be measured by the correlation or coherence time τ_c, which is defined as

$$\tau_c = \int_0^\infty \frac{\langle \delta A(t)\delta A(0)\rangle_c}{\langle |\delta A(0)|^2\rangle_c} dt \tag{1.176}$$

If one assumes a markovian process, i.e. no memory of the system, all time-correlation functions higher than $\mathfrak{C}_A(t)$ are zero. Then the time-correlation function of $\delta A(t)$ decays as a single exponential with relaxation time τ_r, so that

$$\langle \delta A(t)\delta A(0)\rangle_c = \langle |\delta A(0)|^2\rangle_c \times e^{-t/\tau_r} \tag{1.177}$$

then $\tau_c = \tau_r$ and equation (1.176) provides a proper method of determining the correlation time, which rapidly vanishes for $t > \tau_c$.

According to the **Wiener-Khintchine Theorem** the spectral power density for the stationary random variable $A(t)$ is defined as the Fourier transform of the time-correlation function $\mathfrak{C}_A(t)$:

$$I_A(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega\tau}\langle A(\tau)A^*(0)\rangle_c d\tau \tag{1.178}$$

2 Waves and particles

2.1 Photons

Electromagnetic radiation (light) behaves in interference experiments as if it were a wave and in other circumstances, such as the photoelectric effect or Compton effect, it behaves if it were composed of particles. These particles, called photons, carry the discrete amount of energy E and other properties associated with the wave.

$$\text{Energy} \quad E = h\nu = \frac{hc}{\lambda} \tag{2.1}$$

$$\text{Momentum} \quad \overrightarrow{p} = \hbar\overrightarrow{k} = \frac{E}{c}\mathbf{k} = \frac{h\nu}{c}\mathbf{k} = \frac{h}{\lambda}\mathbf{k} \tag{2.2}$$

$$\text{Rest mass} \quad m = 0 \tag{2.3}$$

$$\text{Spin 1} \quad \hbar = \frac{h}{2\pi} \tag{2.4}$$

There are different energy and wavelength units used in the field of atomic and molecular processes, such as electron volts $[eV]$ and wavenumbers $[cm^{-1}]$.

$$E[\text{eV}] = \frac{12398}{\lambda[\mathring{\text{A}}]} \tag{2.5}$$

$$E[\text{eV}] = 2.418 \times 10^{14}\nu[\text{Hz}] \tag{2.6}$$

$$\bar{\nu}[\text{cm}^{-1}] = \frac{10^4}{\lambda[\mu\text{m}]} \tag{2.7}$$

$$1\ m_e = 9,11 \times 10^{-31}\text{kg} = 511\frac{\text{keV}}{c^2} \tag{2.8}$$

$$1\ \text{eV} = 1.602 \times 10^{-19}\text{J} \tag{2.9}$$

2.2 Compton effect

The Compton effect (A.H. Compton 1923) describes the wavelength shift of incident radiation after the 'collision' of photons or electromagnetic waves with loosely bound (nearly free) electrons. In the experimental set-up a nearly monochromatic electromagnetic x-ray beam with ($\lambda_0 \approx 1\mathring{\text{A}}$) was used to irradiate a graphite target. The intensity of the scattered radiation was measured as a function of scattering angle and wavelength. The results, illustrated in Fig. (2.2), showed that although part of the scattered radiation had the same wavelength λ_0 as the incident radiation, there was also a second component of wavelength λ_1, where $\lambda_1 > \lambda_0$. The shift in wavelength between the incident and scattered radiation, $\Delta\lambda = \lambda_0 - \lambda_1$ called *Compton shift* could not be explained by the classical models. Classical models would predict the induced dipoles to oscillate and emit with the frequency of the incident radiation and thus no wavelength shifts

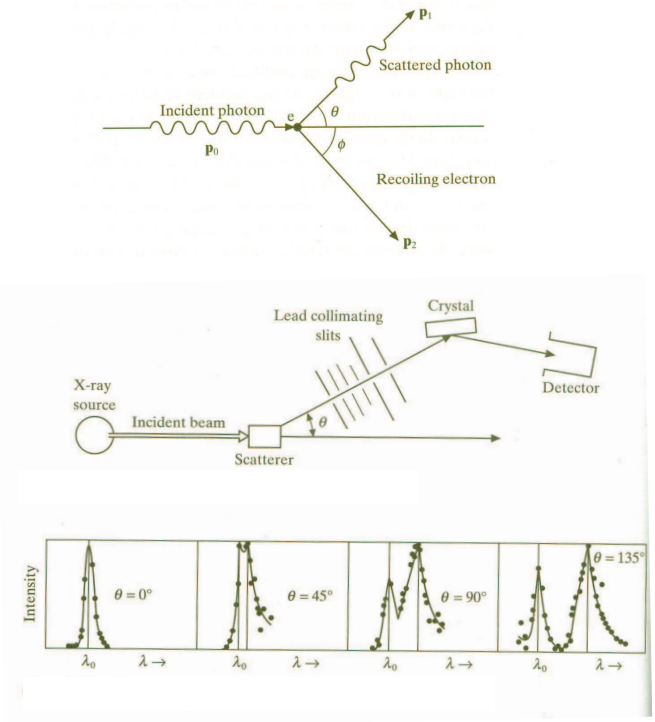


Abbildung 2.1. Set up and scattering pattern of photons as a function of wavelength. The data were taken for graphite crystals.

should be observed $\Delta\lambda = 0$. The observed shift in wavelength was found to vary with the angle of scattering and to be proportional to $\sin^2(\theta/2)$ where θ is the scattering angle. Moreover, the Compton shift was independent of both the material used as a scatterer and λ_0, and the value of the constant of proportionality was 0.048×10^{-10}m. The results were interpreted with relativistic kinematics and the use of momentum and energy conservation, with $\overrightarrow{p_0}$, the momentum of the photon before interaction, $\overrightarrow{p_1}$ and $\overrightarrow{p_2}$ the momentum of the photon and electron, respectively, after interaction, E_0 the energy of the photon, mc^2 the rest mass of the electron (here we assume a free electron with momentum zero), E_1 and E_2

the photon and electron energy, respectively after interaction:

$$\begin{aligned}
\overrightarrow{p_0} &= \overrightarrow{p_1} + \overrightarrow{p_2} && (2.10)\\
E_0 + m_e c^2 &= E_1 + E_2 = \frac{hc}{\lambda_1} + \sqrt{m_e^2 c^4 + p_2^2 c^2} && (2.11)\\
\overrightarrow{p_2} &= \overrightarrow{p_0} - \overrightarrow{p_1} && (2.12)\\
p_2^2 &= \overrightarrow{p_2} \bullet \overrightarrow{p_2} = p_0^2 + p_1^2 - 2p_0 p_1 \cos(\theta) && (2.13)\\
E_0 - E_1 &= c(p_0 - p_1) = \sqrt{m_e^2 c^4 + p_2^2 c^2} - m_e c^2 && (2.14)\\
m_e^2 c^4 + p_2^2 c^2 &= m_e^2 c^4 + 2m_e c^3 (p_0 - p_1) + c^2 (p_0 - p_1)^2 && (2.15)\\
p_2^2 &= (p_0 - p_1)^2 + 2m_e c(p_0 - p_1) && (2.16)\\
2m_e c(p_0 - p_1) &= -p_0^2 - p_1^2 + 2p_0 p_1 + p_0^2 + p_1^2 - 2p_0 p_1 \cos(\theta) && (2.17)\\
m_e c(p_0 - p_1) &= p_0 p_1 (1 - \cos(\theta)) = 2p_0 p_1 \sin^2(\frac{\theta}{2}) && (2.18)\\
m_e c(\frac{1}{p_1} - \frac{1}{p_0}) &= 2\sin^2(\frac{\theta}{2}) && (2.19)\\
\frac{m_e c}{h}(\lambda_1 - \lambda_0) &= 2\sin^2(\frac{\theta}{2}) && (2.20)
\end{aligned}$$

$$\Delta\lambda = \lambda_1 - \lambda_0 = 2\frac{h}{m_e c}\sin^2(\frac{\theta}{2}) = 2\lambda_c \sin^2(\frac{\theta}{2}) \geq 0. \quad (2.21)$$

The wavelength $\lambda_c = \frac{h}{m_e c}$ is called the Compton wavelength, and a photon with Compton wavelength λ_c has the energy of the rest mass of the electron $m_e c^2 = 511\,\mathrm{keV}$

$$E_{ph} = \frac{hc}{\lambda_c} = \frac{hc \cdot m_e c}{h} = m_e c^2. \quad (2.22)$$

The value of $\lambda_c = 0.02426 \times 10^{-10}\mathrm{m} \approx 0.024\text{Å}$ is independent of λ_0 and the material of the scatterer and in very good agreement with the observed value. The existence of the unmodified component of the scattered radiation, which has the same wavelength λ_0 as the incident radiation, can be explained by scattering from electrons so tightly bound that the entire atom ($M \gg m_e$) recoils and the Compton shift is negligible.

The Compton effect is a nice experiment to demonstrate the particle character of electromagnetic waves. On the other hand the wave behaviour of particles has also been demonstrated, i.e. by observing the diffraction of electrons from edges of slits (Fig. 2.2) and from scattering by a crystal (Fig. 2.2). According to de Broglie (1924) all material particles possess wave-like characteristics. The wavelength associated with particles is given by

$$\lambda = \frac{h}{p}. \quad (2.23)$$

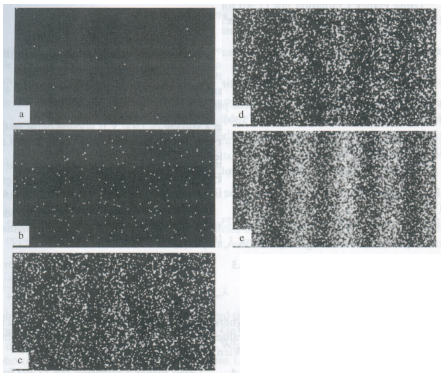


Abbildung 2.2. Build up of an interfernce pattern by accumulating single electrons in a two-slit experiment of Tonomura et al. (Tonomura, J. et al. *American Journal of Physics* **57**, 117, 1989). Number of electrons: (a) 10; (b) 100; (c) 3000; (d) 20000; (e) 70000.

The wave aspect is also reflected in Bohr's atomic model, characterized by Bohr's postulate

$$2\pi r = n\lambda, \quad \text{n} = 1, 2, 3, \ldots \tag{2.24}$$

$$L = rp \tag{2.25}$$

that the orbital angular momentum L is quantised.

$$L = \frac{n\lambda p}{2\pi} = \frac{nhp}{2\pi p} = n\hbar \tag{2.26}$$

This mechanistic picture, which is an extension to the classical planetary model, gives reasonable values for the energy levels of atoms, but is limited for deriving properties.

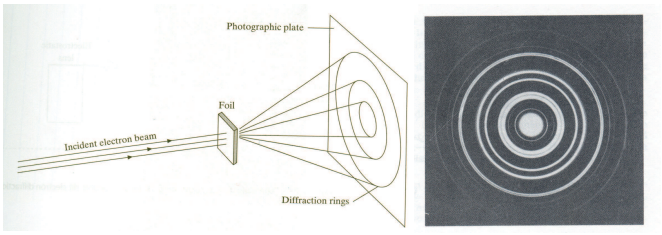


Abbildung 2.3. Set up and diffraction pattern of an electron diffraction experiment on crystal powder (from L. Germer).

$$E_n - E_m = h(\nu_n - \nu_m) = -\frac{m_e}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \tag{2.27}$$

$$a_0 = \frac{(4\pi\varepsilon_0)\hbar^2}{m_e e^2} = 5.29177 \times 10^{-11}\text{m}, \quad \text{Bohr's radius} \tag{2.28}$$

Davisson and Germer confirmed (1925) equation (2.23) by measuring the constructive interference of electrons. The electrons were accelerated by a potential of voltage V, resulting in an electron kinetic energy of $E = eV$.

$$\frac{p^2}{2m_e} = eV \tag{2.29}$$

$$p = \sqrt{2m_e eV} \tag{2.30}$$

$$\lambda = \frac{h}{\sqrt{2m_e eV}} \tag{2.31}$$

$$\lambda[\mathring{\text{A}}] = \frac{12.3}{\sqrt{E[\text{eV}]}} \tag{2.32}$$

At a potential of 100 V the resulting wavelength is $\lambda = 1.23\mathring{\text{A}}$, and diffraction effects should appear at $d \approx \lambda$. Davisson and Germer observed the reflected low energy electrons (< 400 eV) from a Ni crystal to show constructive interference at specific angles θ_n (LEED: Low energy electron diffraction)

$$n\lambda = d\sin(\theta_n). \tag{2.33}$$

At energies of 54 eV the observed angle for n = 1 was found to be $\theta_1 = 50°$. With $d = 2.15\mathring{\text{A}}$, known from x-ray diffraction experiments on Ni one can calculate the wavelengths to be

$$\lambda = 2.15(\sin(50°))\ \mathring{\text{A}} = 1.65\ \mathring{\text{A}} \tag{2.34}$$

$$\lambda = \frac{h}{\sqrt{2m_e eV}} = \frac{12.3}{\sqrt{54}}\ \mathring{\text{A}} = 1.67\ \mathring{\text{A}} \tag{2.35}$$

Electron diffraction experiments in transmission on thin Au and Pt films were performed by G.P. Thomson (1927). He used powder samples of very small crystals, so that the orientations of crystal axes were isotropically distributed. The measured transmission powder spectrum has axial symmetry and shows Debye-Scherrer rings (Fig. 2.2), similar x-ray diffraction experiments. The electron diffraction pattern can be explained with the Bragg condition (2.33). Since the spatial resolution of experiments depend on the wavelength of the detecting particles, the short wavelength of electrons, which can be in the range of 1 Å, are used for electron diffraction and electron microscopy experiments resolving structural details on atomic or molecular scales.

The properties of electrons were always an important issue in physics: J.J. Thomson was awarded the Nobel Prize for showing that the electron is a particle. G.P. Thomson, his son, was awarded the Prize for showing that the electron is a wave.

Neutral particles, such as neutrons and He-atoms, show also wave properties

with different wavelengths, depending on their rest mass and velocity. The kinetic energy of neutrons can easily be moderated by scattering in a medium of specific temperature. Water is an efficient neutron scatterer and is often used to reduce the average kinetic energy of neutrons to room temperature

$$\overline{E} = \frac{3}{2}k_B T \tag{2.36}$$

$$k_B T \approx \frac{1}{40}\,\mathrm{eV}, \quad at\ T = 293\,\mathrm{K} \tag{2.37}$$

A crystal lattice can be used to select a monochromatic wavelength

$$\lambda_n = \frac{h}{p_n} = \frac{h}{\sqrt{2m_n \frac{3}{2}k_B T}} \tag{2.38}$$

Since the mass of neutrons is much bigger than the electron mass $\frac{m_n}{m_e} \approx 1800$, thermal neutrons have the appropriate wavelength for structures with distances or lattice constants of $d \approx 1 \ldots 10$ Å. Neutrons are especially useful for scattering experiments with hydrogen atoms.

2.3 Plane waves, free particles

For an electromagnetic plane wave or photons the following equations hold

$$E(x,t) = e^{i(\vec{k}\bullet\vec{x}-\omega t)} \tag{2.39}$$

$$\vec{p} = \frac{h}{\lambda}\mathbf{p} = \frac{h\vec{k}}{2\pi} = \hbar\vec{k} \tag{2.40}$$

$$E = h\nu = h\frac{\omega}{2\pi} = \hbar\omega \tag{2.41}$$

$$E(x,t) = e^{\frac{i}{\hbar}(\vec{p}\bullet\vec{x}-Et)} \tag{2.42}$$

$$E = pc \tag{2.43}$$

$$\omega = kc \tag{2.44}$$

Equation (2.39) is a solution of the homogeneous wave equation

$$\frac{\partial^2 E(x,t)}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2 E(x,t)}{\partial t^2} = 0, \tag{2.45}$$

since inserting (2.39) gives

$$-k^2 - \frac{1}{c^2}(-\omega^2) = 0 \tag{2.46}$$

and this is the correct dependence of $E(p)$ and $\omega(k)$. Note, that for the wave equation eigenvalues exist for E, p, and p^2, but not for x and t.

For plane material waves or a free particle with non vanishing rest mass we have

$$\overrightarrow{p} = \frac{h}{\lambda}\mathbf{p} = \hbar\overrightarrow{k} \tag{2.47}$$

$$E = h\nu = \hbar\omega \tag{2.48}$$

$$E = \frac{p^2}{2m} \tag{2.49}$$

$$\omega = \frac{\hbar k^2}{2m} \tag{2.50}$$

Now we end up in analogy with a material wave function $\psi(x,t)$

$$\psi(x,t) = e^{i(\overrightarrow{k}\bullet\overrightarrow{x}-\omega t)} \tag{2.51}$$

$$\psi(x,t) = e^{\frac{i}{\hbar}(\overrightarrow{p}\bullet\overrightarrow{x}-Et)} \tag{2.52}$$

To guess a wave equation like (2.45) for a free particle in analogy to $E = \frac{p^2}{2m}$ we choose the second derivative in x and a first derivative in t:

$$\frac{\partial\psi(x,t)}{\partial x} = \frac{i\overrightarrow{p}}{\hbar}\psi(x,t) \tag{2.53}$$

$$\frac{\partial^2\psi(x,t)}{\partial x^2} = -\frac{p^2}{\hbar^2}\psi(x,t) \tag{2.54}$$

$$\frac{\partial\psi(x,t)}{\partial t} = -\frac{iE}{\hbar}\psi(x,t). \tag{2.55}$$

Since we have a relation between energy and momentum (2.49) the guessed wave equation for a particle, which fulfill this equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} = i\hbar\frac{\partial\psi(x,t)}{\partial t}. \tag{2.56}$$

Here, also Eigenvalues exist for values of E, p, and p^2, but not for x and t. Generalization for a bound particle with a potential V and the force $\overrightarrow{F}$ with

$$\overrightarrow{F} = -\overrightarrow{\nabla}V \tag{2.57}$$

and

$$\frac{p^2}{2m} + V(x) = E \tag{2.58}$$

gives

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x)\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t}, \quad 1-D \tag{2.59}$$

$$-\frac{\hbar^2}{2m}\triangle\psi(\overrightarrow{r},t) + V(\overrightarrow{r})\psi(\overrightarrow{r},t) = i\hbar\frac{\partial\psi(\overrightarrow{r},t)}{\partial t}, \quad 3-D. \tag{2.60}$$

This equation is called **Schrödinger equation**. It is a linear and homogeneous partial differential equation, and in analogy to the wave equation the *superposition principle* holds.

$$\psi_1,\ \psi_2 \ \text{solutions} \Rightarrow\ c_1\psi_1 \pm c_2\psi_2 \quad \text{solutions} \tag{2.61}$$

If ψ_1 and ψ_2 are solutions of the Schrödinger equation (SE), then the sum and the difference of both $\psi_1 \pm \psi_2$ are also solutions of the SE. This is the fundamental basis for interference effects. Solutions of the SE are found in $\mathfrak{L}^2$: quadratic integrable functions. Moreover, they should vanish for plus and minus infinity.

A plane wave has momentum $\overrightarrow{p}(\overrightarrow{k})$, but it is *not localized*. A plane wave has an infinite length, but a precise momentum. Therefore it is not possible to calculate a probability of finding a plane wave at a specific position (no normalization). Nevertheless, taken into account the superposition principle every function of $\mathfrak{L}^2$ can be represented by a weighted sum of plane waves. For convenience purposes, we go on calculating in one dimensional without limiting the generality:

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k,\omega) e^{i(kx-\omega t)} dk. \tag{2.62}$$

Every function $\psi(x,t)$ can be described as an infinite sum of plane waves (remember Fourier transformation), and the amplitude function of the wave vectors $A(k)$ gives the weighting of the individual plane waves. The amplitude function can be calculated by the inverse Fourier transformation

$$A(k,\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x,t) e^{-i(kx-\omega t)} dx. \tag{2.63}$$

A simple example is the sum of two cosine functions of the same amplitude as shown in Fig. (2.3).

$$\psi(x,t) = e^{i(k_1 x-\omega_1 t)} + e^{i(k_2 x-\omega_2 t)} \tag{2.64}$$

$$= e^{i\left[\left(\frac{k_1+k_2}{2}\right)x-\left(\frac{\omega_1+\omega_2}{2}\right)t\right]} \times 2\cos\frac{1}{2}(\Delta k x - \Delta\omega t) \tag{2.65}$$

By increasing the number of waves a more localized wavepacket with less spikes can be generated (Fig. 2.3). Since $\omega = \omega(k)$ with $\omega(k) = \frac{\hbar k^2}{2m}$ for a free particle, a distribution $A(k)$ (see Fig. 2.3) is equivalent to a distribution of frequencies. If we develop $\omega(k)$ around k_0, where $\omega(k_0) = \omega_0$:

$$\omega(k) = \omega_0 + (k-k_0)\frac{d\omega}{dk}|_{k_0} + \ldots \tag{2.66}$$

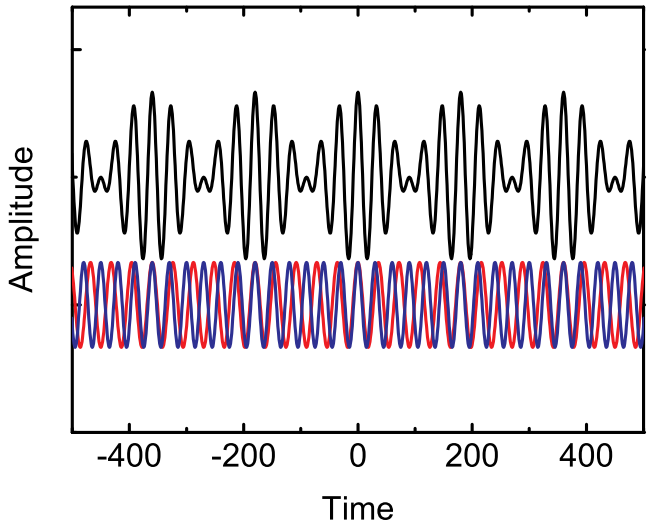


Abbildung 2.4. Sum of two cosine waves of the same amplitude and $\omega_1 = 0.1745s^{-1}$ and $\omega_1 = 0.2094s^{-1}$. The amplitude is plotted versus time.

and insert this into (2.62) it becomes

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i(k_0 x - \omega_0 t)} A(k,\omega) e^{i[(k-k_0)x - (k-k_0)\frac{d\omega}{dk}|_{k_0} t]} dk \tag{2.67}$$

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} e^{i(k_0 x - \omega_0 t)} \int_{-\infty}^{\infty} A(k,\omega) e^{i(k-k_0) f(x - \frac{d\omega}{dk}|_{k_0} t)} dk. \tag{2.68}$$

This means a wavepacket can be described as a product of a plane wave at k_0 and carrier frequency ω_0, which is moving with the phase velocity v_{ph} and an envelope $f(x - \frac{d\omega}{dk}|_{k_0} t)$, which is moving with the group velocity v_{gr}.

$$v_{ph} = \frac{\omega_0}{k_0} \tag{2.69}$$

$$v_{gr} = \frac{d\omega}{dk}|_{k_0} \tag{2.70}$$

$$\overrightarrow{v_{gr}} = \overrightarrow{\nabla}_k \omega(k) \tag{2.71}$$

We can characterize the velocity of the particle or wavepacket by the group velocity v_{gr}:

$$\omega(k) = \frac{\hbar k^2}{2m} \Rightarrow v_{gr} = \frac{2\hbar k}{2m} = \frac{\hbar k}{m} = \frac{p_0}{m} \Rightarrow v_{gr} = \frac{p_0}{m} \tag{2.72}$$

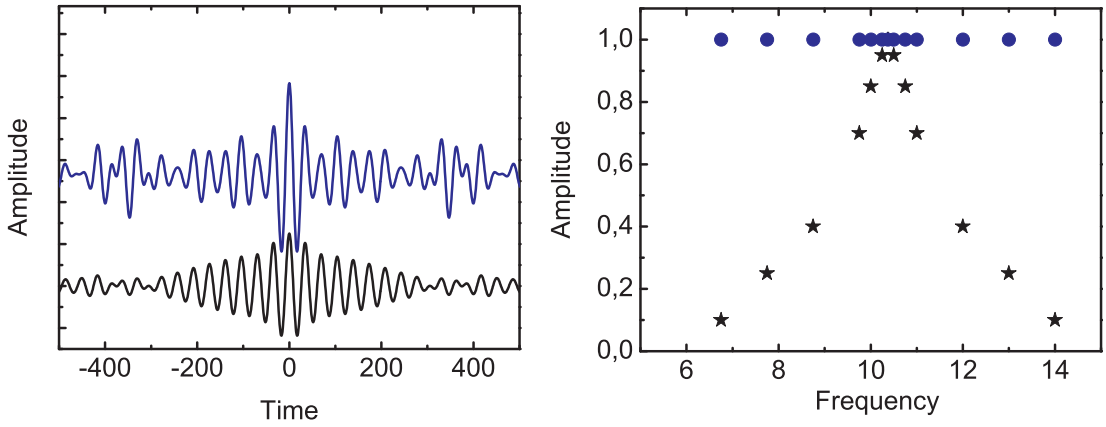


Abbildung 2.5. Left: Sum of several cosine waves of same (blue) and different (black) amplitudes. Right: Amplitude distributions.

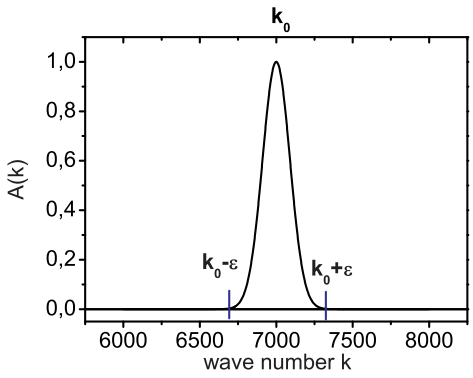


Abbildung 2.6. Fourier components centered around k_0.

That is exactly what we expect for the velocity of a free particle. If we have an amplitude function of wave vectors $A(k)$ constant in the range from $k_0 - \Delta k$ to $k_0 + \Delta k$

$$A(k) = \begin{cases} \frac{1}{2\Delta\hat{k}} & , \quad k_0 - \Delta k < k < k_0 + \Delta k \\ 0 & , \quad else \end{cases} \tag{2.73}$$

Then we get

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} e^{i(k_0 x - \omega_0 t)} \int_{k_0-\Delta\hat{k}}^{k_0+\Delta\hat{k}} A(k) e^{i(k-k_0)[x - \frac{d\omega}{dk}|_{k_0} t]} dk \tag{2.74}$$

$$\overset{k'=k-k_0}{=} \frac{1}{\sqrt{2\pi}} e^{i(k_0 x - \omega_0 t)} \int_{-\Delta\hat{k}}^{\Delta\hat{k}} \frac{1}{2\Delta\hat{k}} e^{ik'[x - \frac{d\omega}{dk'}|_0 t]} dk' \tag{2.75}$$

$$\overset{\alpha = x - \frac{d\omega}{dk'} t}{=} e^{i(k_0 x - \omega_0 t)} \frac{1}{2\Delta\hat{k} i\alpha\sqrt{2\pi}} \left[e^{ik'\alpha} \right]_{-\Delta\hat{k}}^{\Delta\hat{k}} \tag{2.76}$$

$$= e^{i(k_0 x - \omega_0 t)} \frac{1}{2\Delta\hat{k} i\alpha\sqrt{2\pi}} \left[e^{i\Delta\hat{k}\alpha} - e^{-i\Delta\hat{k}\alpha} \right] \tag{2.77}$$

$$= e^{i(k_0 x - \omega_0 t)} \frac{1}{\sqrt{2\pi}} \frac{\sin(\Delta k \alpha)}{\Delta k \alpha} \tag{2.78}$$

$$\psi(x,t) = e^{i(k_0 x - \omega_0 t)} \frac{1}{\sqrt{2\pi}} \mathrm{sinc}(\Delta k [x - \frac{d\omega}{dk} t]) \tag{2.79}$$

Equation (2.79) describes the wavepacket of a particle. As a direct conclusion from the Fourier transformation taking $\frac{2\pi}{\Delta k}$ as the wave vector width we get:

$$\Delta x = \frac{2\pi}{\Delta k} \Rightarrow \Delta x \cdot \Delta k = 2\pi \Rightarrow \Delta x \cdot \Delta p_x = 2\pi\hbar \tag{2.80}$$

This reciprocal relation between the spread in space and momentum (or time

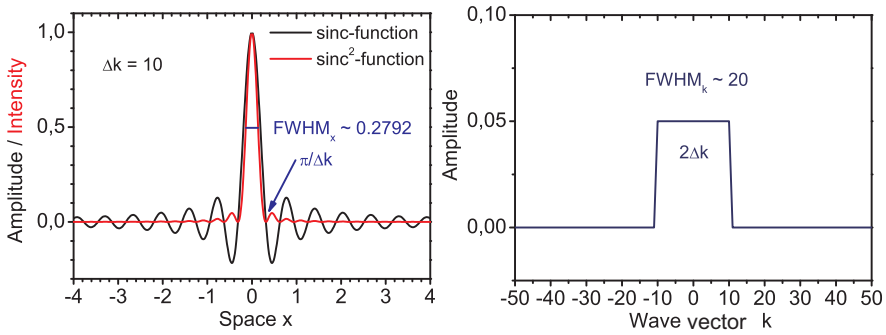


Abbildung 2.7. Left: Amplitude of a sinc function (black) and its intensity (blue). Right: A(k) of the distribution.

and energy) is fundamental and varies with the distribution functions of $A(k)$. For all distribution functions it is

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}$$
$$\Delta t \cdot \Delta E \geq \frac{\hbar}{2}. \tag{2.81}$$

These relations are examples of the *uncertainty principle* and gives an upper limit for the localization of space and momentum or time and energy. Note, space and time are not eigenvalues of the SE, and they are directly connected with momentum and energy via the differential equations.

In equation (2.72) the group velocity of a particle is determined by its rest mass. For photons the rest mass is zero, and the group velocity is given by

$$v_{gr} = \frac{d\omega}{dk}|_{k_0} = \frac{dkc}{dk}|_{k_0} = c. \tag{2.82}$$

The wavepacket consisting of photons has a group velocity c, and is not spreading out in time. This situation changes if the photon wavepacket, which is a temporally short and spectrally broad pulse, is travelling through a dispersive medium with $n = n(\lambda)$ and the dielectric constant ϵ. If that is the case, the wave vector becomes dependent on the frequency

$$k^2(\omega) = \frac{\omega^2}{c^2}\epsilon(\omega) = \frac{\omega^2}{c^2}n^2(\omega) \tag{2.83}$$

$$k(\omega) = k_0 + \frac{dk}{d\omega}|_{\omega_0}(\omega - \omega_0) + \frac{1}{2}\frac{d^2k}{d\omega^2}|_{\omega_0}(\omega - \omega_0)^2 + \cdots = k_0 + \delta k \tag{2.84}$$

$$v_{gr} = \left(\frac{dk}{d\omega}|_{\omega_0}\right)^{-1} \tag{2.85}$$

The term

$$\frac{d^2k}{d\omega^2}|_{\omega_0} = -\frac{1}{v_{gr}^2}\frac{dv_{gr}}{d\omega}|_{\omega_0} = \mathrm{GVD}(\omega) \tag{2.86}$$

is the group velocity dispersion (GVD) parameter and is useful for calculating the change of transit time for a broadband pulse as a function of frequency through a medium or an optical setup. Alternatively, it is also possible to look at the complex phase in the frequency domain and define the GVD as the second derivative of the phase with respect to frequency. The units of the GVD is $[\frac{s^2}{m}]$ or $[\frac{\text{time}}{\text{length}\cdot\text{bandwidth}}] = [\frac{fs}{cm\cdot fs^{-1}}]$. It is useful to represent the properties of the complex electric field $E^+(t)$ of short light pulses by the product of a complex envelope function $\mathcal{E}(t)$ and a phase term:

$$E^+(t) = \frac{1}{2}\mathcal{E}(t)e^{i\Phi(t)} = \frac{1}{2}\mathcal{E}(t)e^{i\phi(t)}e^{i\omega_0 t} \tag{2.87}$$

Here, the plus at the electric field indicate only positive frequencies, $\phi(t)$ is the time dependent phase and ω_0 the frequency expectation value of the electric field. In most practical cases of interest the spectral amplitude is centered around ω_0 and has non negligible amplitudes only in a small frequency range $\Delta\omega$, with

$$\frac{\Delta\omega}{\omega_0} \ll 1. \tag{2.88}$$

For inequality (2.88) to be satisfied, the temporal variation of $\mathcal{E}(t)$ and $\phi(t)$ within an optical cycle $T = \frac{2\pi}{\omega_0}$ has to be small ($T \approx 2\,fs$ for visible radiation). The

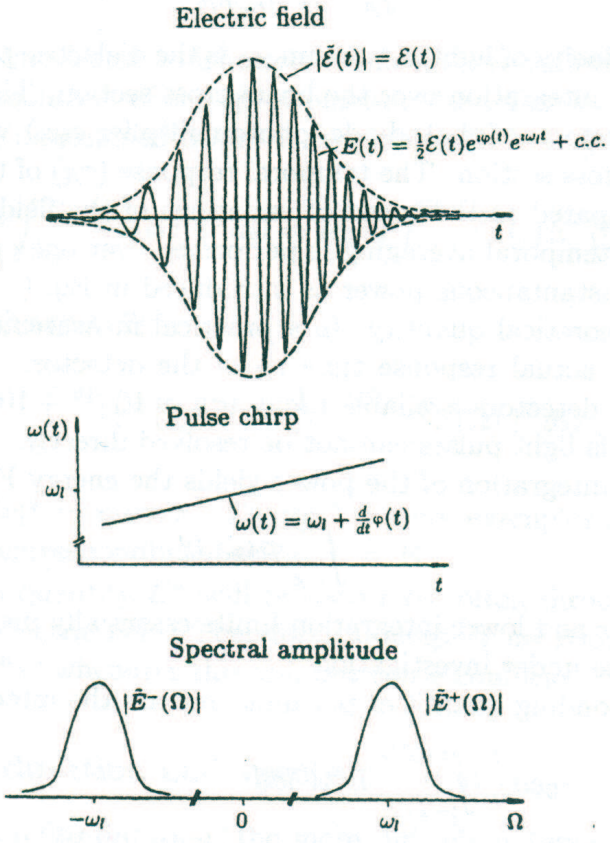


Abbildung 2.8. Electric field, time dependent carrier frequency and spectral amplitude of an upchriped pulse.

physical meaning of the phase function $\Gamma(t)$ is the following. The first derivative of the phase funtion $\Gamma(t)$ is the time dependent carrier frequency choosen such as to minimize the variation of phase $\phi(t)$.

$$\omega(t) = \omega_0 + \frac{d}{dt}\varphi(t). \tag{2.89}$$

For $\frac{d\phi}{dt} = b = \text{const}$, a non-zero value of b just means a correction of the carrier frequency, which is now $\omega = \omega_0 + b$. For $\frac{d\phi}{dt} = f(t)$, the carrier frequency varies

with time and the corresponding pulse is said to be frequency modulated or chirped. For $\frac{d^2\phi}{dt^2} > 0$, the carrier frequency increases along the pulse, which is then called up chirped (Fig. 2.3). If the carrier frequency decreases along the pulse it is called down chirped.

The pulse duration and spectral width of a short light pulse is essential to follow short (femtosecond) atomic and molecular dynamics. For very short and spectrally broad light pulses it is difficult to determine the exact pulse shape of a light pulse. For single pulses, the typical representative function that is readily accessible to the experimentalist is the intensity autocorrelation:

$$A_{int}(\tau) = \int_{-\infty}^{\infty} I(t)I(t-\tau)dt. \tag{2.90}$$

This is by definition a symmetric function $A_{int}(\tau) = A_{int}(-\tau)$ and its Fourier transform is given by the real function:

$$A_{int}(\Omega) = \widetilde{I}(\Omega)\widetilde{I}^*(\Omega). \tag{2.91}$$

The most commonly cited pulse profiles are the Gaussian, for which the temporal dependence of the field is:

$$\mathcal{E}(t) = \mathcal{E}_0 e^{-(t/\tau_G)^2} \tag{2.92}$$

and the secant hyperbolic

$$\mathcal{E}(t) = \mathcal{E}_0 \mathrm{sech}(t/\tau_s) = \mathcal{E}_0 \frac{2}{e^{(t/\tau_s)} + e^{-(t/\tau_s)}} \tag{2.93}$$

with the parameters $\tau_G = \tau_p \frac{1}{\sqrt{2\ln 2}}$ and $\tau_s = \tau_p \frac{1}{1.76}$. Since, the coherent temporal and spectral characteristics of the **fields** (and not intensities) are related to each other through Fourier transforms, the bandwidth $\Delta\omega_p$ and pulse duration τ_p cannot vary independently of each other. There is a minimum duration-bandwidth product:

$$\Delta\omega_p \tau_p = 2\pi \Delta\nu_p \tau_p \geq 2\pi c_B \tag{2.94}$$

The numerical constant c_B is called the duration-bandwidth product and is on the order of 1, depending on the actual pulse shape. The values of $\Delta\omega_p$ and τ_p are given by the FWHM (Full Width at Half Maximum) values. If the pulse shape is complex one can introduce different definitions as for example $\tau_p^2 = (\langle t^2 I(t)\rangle - \langle tI(t)\rangle^2)^2$, using the second moment.

For some pulse shapes the duration-bandwidth product becomes

Gaussian pulse shapes

$$I(t) \propto e^{-1/2(t/\tau_G)^2} \tag{2.95}$$
$$\tau_p = \tau_G 2\sqrt{\ln 2} \tag{2.96}$$
$$I(\omega) \propto e^{-(\omega\tau_G)^2/2} \tag{2.97}$$
$$\Delta\omega_p = \frac{2\sqrt{\ln 2}}{\tau_G} \tag{2.98}$$
$$c_B \approx 0.441 \tag{2.99}$$

Sech pulse shapes

$$I(t) \propto \mathrm{sech}^2(t/\tau_s) \tag{2.100}$$
$$\tau_p \approx 1.763\tau_s \tag{2.101}$$
$$I(\omega) \propto \mathrm{sech}^2(\pi\omega\tau_s/2) \tag{2.102}$$
$$\Delta\omega_p \approx \frac{1.122}{\tau_s} \tag{2.103}$$
$$c_B \approx 0.315 \tag{2.104}$$

Lorentian pulse shapes

$$I(t) \propto \frac{1}{(1+(t/\tau_L)^2)^2} \tag{2.105}$$
$$\tau_p \approx 1.287\tau_L \tag{2.106}$$
$$I(\omega) \propto e^{-2(|\omega|\tau_L)} \tag{2.107}$$
$$\Delta\omega_p \approx \frac{0.693}{\tau_L} \tag{2.108}$$
$$c_B \approx 0.142 \tag{2.109}$$

Note, this equations hold for the **intensity profiles** of a bandwidth limited pulse, and the duration-bandwidth product is given for the **fields** (factor $\sqrt{2}$). If we introduce a linear chirp to a gaussian profile we get:

$$\mathcal{E}(t) = \mathcal{E}_0 e^{-(1+ia)(t/\tau_G)^2} \tag{2.110}$$
$$\frac{d\varphi}{dt} = \frac{-2at}{\tau_G^2} \tag{2.111}$$
$$\Rightarrow \Delta\nu_p\tau_p = \frac{2\ln 2}{2\pi}\sqrt{1+a^2} \tag{2.112}$$
$$\widetilde{I}(\omega) \propto \frac{\mathcal{E}_0^2\tau_G^2}{\sqrt{1+a^2}} e^{-\frac{\omega^2\tau_G^2}{2(1+a^2)}}. \tag{2.113}$$

Upon introducing linear chirp to a bandwidth limited pulse the pulse duration will become longer.

3 Schrödinger equation

The SE (3.1) is a partial differential equation describing the dynamics of the wave function $\psi(\overrightarrow{r},t)$.

$$-\frac{\hbar^2}{2m}\triangle\psi(\overrightarrow{r},t)+V(\overrightarrow{r})\psi(\overrightarrow{r},t)=i\hbar\frac{\partial\psi(\overrightarrow{r},t)}{\partial t} \tag{3.1}$$

To interpret the meaning of the wave function $\psi(\overrightarrow{r},t)$ we must remember that $\psi(\overrightarrow{r},t)$ is in general a complex function and $|\psi(\overrightarrow{r},t)|$ is large where the particle is likely to be found. The diffraction pattern made by light depend on the intensity of the electric field, which is $\propto |E(\omega,t)|^2$. In similar way, M. Born made the fundamental postulate (1926), that if a particle is described by a wave function $\psi(\overrightarrow{r},t)$ the probability of finding the particle within the volume element $d\overrightarrow{r}=dxdydz$ about the point $\overrightarrow{r}$ at time t is given by:

$$P(\overrightarrow{r},t)=|\psi(\overrightarrow{r},t)|^2d\overrightarrow{r}=\psi^*(\overrightarrow{r},t)\psi(\overrightarrow{r},t)d\overrightarrow{r}. \tag{3.2}$$

Here $P(\overrightarrow{r},t)$ is the (position) probability density. Since the probability of finding a particle somewhere must be unity the normalization relation must hold:

$$\int_{-\infty}^{\infty}\psi^*(\overrightarrow{r},t)\psi(\overrightarrow{r},t)d\overrightarrow{r}=1. \tag{3.3}$$

Note, that $|\psi(\overrightarrow{r},t)|^2$ is the physical quantity that is directly related to the experimental observable quantities.

3.1 Expectation values

If we consider a normalized wave function $\psi(\overrightarrow{r},t)$, then the *average* or *expectation value* of any function $f(\overrightarrow{r})$ is defined as:

$$\langle f(\overrightarrow{r})\rangle=\langle\psi^*(\overrightarrow{r},t)|f(\overrightarrow{r})\psi(\overrightarrow{r},t)\rangle=\int_{-\infty}^{\infty}\psi^*(\overrightarrow{r},t)f(\overrightarrow{r})\psi(\overrightarrow{r},t)d\overrightarrow{r}. \tag{3.4}$$

If we want to calculate the probability to find a particle described by $\psi(\overrightarrow{r},t)$ at the position $\overrightarrow{r}$, we have to set $f(\overrightarrow{r})=\overrightarrow{r}$, and then the expectation value for finding the particle at position $\overrightarrow{r}$ is given by:

$$\langle\overrightarrow{r}\rangle=\langle\psi^*(\overrightarrow{r},t)|\overrightarrow{r}\psi(\overrightarrow{r},t)\rangle=\int_{-\infty}^{\infty}\psi^*(\overrightarrow{r},t)\overrightarrow{r}\psi(\overrightarrow{r},t)d\overrightarrow{r}. \tag{3.5}$$

Since in experiments all observed quantities are expectation values, the integral or scalar product $\langle f(\overrightarrow{r})\rangle$ is necessary to connect the SE with physical quantities.

$$\int \psi^*(\overrightarrow{r},t)\Phi(\overrightarrow{r},t)dV = \langle\psi|\Phi\rangle \tag{3.6}$$

The square integrable functions $\psi \in X$ and $\Phi \in X$ together with the following properties of the scalar product $\langle\,|\,\rangle$ define a Hilbert space:

$$\begin{aligned}
\langle\Phi_1+\Phi_2|\psi\rangle &= \langle\Phi_1|\psi\rangle + \langle\Phi_2|\psi\rangle, \quad \forall\Phi_i,\psi\in X && (3.7)\\
\langle\lambda\Phi|\psi\rangle &= \lambda^*\langle\Phi|\psi\rangle, \quad \forall\Phi,\psi\in X,\lambda\in\mathbb{C} && (3.8)\\
\langle\Phi|\psi\rangle &= \langle\psi|\Phi\rangle^*, \quad \forall\Phi,\psi\in X, && (3.9)\\
\langle\psi|\psi\rangle &\geq 0, \forall\psi\in X && (3.10)\\
\langle\psi|\psi\rangle &= 0 \quad\Leftrightarrow\quad \psi = 0. && (3.11)
\end{aligned}$$

The property of becoming complex conjugated upon exchanging the arguments is called sesqi linear. From these properties the Schwarz relation follows:

$$\begin{aligned}
|\langle\Phi|\psi\rangle|^2 &\leq \langle\Phi|\Phi\rangle\langle\psi|\psi\rangle && (3.12)\\
|\langle\Phi|\psi\rangle|^2 &= \langle\Phi|\Phi\rangle\langle\psi|\psi\rangle \Leftrightarrow \Phi = \lambda\psi. && (3.13)
\end{aligned}$$

Note, that the scalar product can also be written as a norm $\|\psi\|$, which is directly connected to a metric. A metric describes specific properties of the space such as calculating and comparing distances.

$$\begin{aligned}
\|\psi\| &\equiv \sqrt{|\langle\psi|\psi\rangle|} && (3.14)\\
\|\Phi+\psi\|^2 &= \langle\Phi+\psi|\Phi+\psi\rangle && (3.15)\\
\|\Phi+\psi\|^2 &\leq (\|\Phi\|+\|\psi\|)^2 && (3.16)
\end{aligned}$$

Note, the scalar product $\langle\psi|A\varphi\rangle = \langle\widetilde{\psi}|\widetilde{A}\widetilde{\varphi}\rangle$ is invariant to the Fourier transformation, with $\widetilde{\psi}$, $\widetilde{\varphi}$, and $\widetilde{A}$ the Fourier transformations of ψ, φ, and A, respectively.

3.2 Time independent SE

The SE is very often abbreviated by

$$\begin{aligned}
H\psi(\overrightarrow{r},t) &= i\hbar\frac{\partial}{\partial t}\psi(\overrightarrow{r},t) && (3.17)\\
H\psi(\overrightarrow{r},t) &= E(\overrightarrow{r},t)\psi(\overrightarrow{r},t) && (3.18)\\
H &= -\frac{\hbar^2}{2m}\triangle + V(\overrightarrow{r},t) && (3.19)\\
\overrightarrow{p} &= \frac{\hbar}{i}\overrightarrow{\nabla} && (3.20)
\end{aligned}$$

where H is called the Hamilton operator with the kinetic energy operator (first term) and the potential operator (second term). The Hamilton operator is known from classical mechanics to describe the energy, and now it is used to describe the quantum mechanical energy by going from variables to operators.

$$H(\overrightarrow{p}, \overrightarrow{q}) \dashrightarrow H(\frac{\hbar}{i}\overrightarrow{\nabla}, \overrightarrow{r}). \tag{3.21}$$

If the Potential operator $V(\overrightarrow{r}, t) = V(\overrightarrow{r})$ does not depend on time, we can use the product solution method to solve the SE:

$$\begin{aligned}
\psi(\overrightarrow{r}, t) &= f(t)\varphi(\overrightarrow{r}) && (3.22)\\
H\psi(\overrightarrow{r}, t) &= f(t)H\varphi(\overrightarrow{r}) = \varphi(\overrightarrow{r})i\hbar\frac{\partial}{\partial t}f(t) && (3.23)\\
\frac{1}{\varphi(\overrightarrow{r})}H\varphi(\overrightarrow{r}) &= i\hbar\frac{1}{f(t)}\frac{\partial}{\partial t}f(t) \quad \forall\overrightarrow{r}, t;\ \varphi(\overrightarrow{r}), f(t) \neq 0 && (3.24)
\end{aligned}$$

Equation (3.24) is only true for all t and $\varphi(\overrightarrow{r})$ if the following holds

$$\begin{aligned}
\frac{1}{\varphi(\overrightarrow{r})}H\varphi(\overrightarrow{r}) &= i\hbar\frac{1}{f(t)}\frac{\partial}{\partial t}f(t) = \text{const.} = E && (3.25)\\
\Rightarrow \frac{1}{\varphi(\overrightarrow{r})}H\varphi(\overrightarrow{r}) &= E && (3.26)\\
\Rightarrow i\hbar\frac{1}{f(t)}\frac{\partial}{\partial t}f(t) &= E && (3.27)\\
\Rightarrow \frac{df(t)}{f(t)} &= \frac{E}{i\hbar}dt && (3.28)\\
\Rightarrow f(t) &= f(0)e^{-\frac{iE}{\hbar}t} && (3.29)\\
\Rightarrow H\varphi_E(\overrightarrow{r}) &= E\varphi_E(\overrightarrow{r}) && (3.30)
\end{aligned}$$

With the product solution method we get separate solutions for the space and time coordinates. As a direct consequence of this the wave function is the direct product of the space wave function $\varphi_E(\overrightarrow{r})$ for a specific energy E and the time wave function or phase function $f(t)$. The eigenfunctions for the space wave functions are given by equation (3.29) and the time dependence by equation (3.30). Thus, the resulting solution of the SE for a Hamilton operator with $V(\overrightarrow{r}, t) = V(\overrightarrow{r})$ is given by

$$\psi(\overrightarrow{r}, t) = e^{-\frac{iE}{\hbar}t}\varphi_E(\overrightarrow{r}). \tag{3.31}$$

Equation (3.31) is the solution of the stationary SE with E representing the energy of the state and $\varphi_E(\overrightarrow{r})$ the time independent wave function. The phase do not contribute to the probability density and therefore, φ_E has very similar properties as ψ:

$$|\psi(\overrightarrow{r}, t)|^2 = |\varphi_E(\overrightarrow{r}, t)|^2 \tag{3.32}$$

3.3 Some properties of operators

In the Hilbert space an operator, such as the momentum operator $\overrightarrow{p} = \frac{\hbar}{i}\overrightarrow{\nabla}$, defines an operation on the wave function. Some operators U are called unitary, if

$$U^*U = UU^* = \mathbf{1} \tag{3.33}$$

some operators N are called normal if

$$N^*N = NN^* \tag{3.34}$$

and most importantly operators H called hermitian or self adjoint if

$$H^* = H. \tag{3.35}$$

For two hermitian operators S and T the following rules hold

$$\begin{aligned}
(S+T)^* &= S^* + T^* && (3.36)\\
(\lambda S)^* &= \lambda^* S^* && (3.37)\\
(TS)^* &= S^*T^* && (3.38)\\
(T^*)^* &= T && (3.39)\\
\langle T\psi|\Phi\rangle &= \langle\psi|T^*\Phi\rangle && (3.40)
\end{aligned}$$

The normalization condition is physical meaningful, because the probability to find an existing particle in the universe should be one. This probability should not change with time, and the time derivative of the normalization condition has to vanish:

$$\begin{aligned}
\frac{d}{dt}\langle\psi|\psi\rangle &= 0 && (3.41)\\
\langle\dot{\psi}|\psi\rangle + \langle\psi|\dot{\psi}\rangle &= 0 && (3.42)\\
\langle\frac{1}{i\hbar}H\psi|\psi\rangle + \langle\psi|\frac{1}{i\hbar}H\psi\rangle &= 0 && (3.43)\\
\frac{1}{i\hbar}\left(-\langle H\psi|\psi\rangle + \langle\psi|H\psi\rangle\right) &= 0 && (3.44)\\
\Rightarrow \langle H\psi|\psi\rangle &= \langle\psi|H\psi\rangle && (3.45)\\
\Rightarrow H^* &= H. && (3.46)
\end{aligned}$$

It follows that the Hamilton operator is hermitian. In addition one can follow from the time independent normalization condition:

$$\int_V |\psi(\overrightarrow{r},t)|^2 dV = 1 \tag{3.47}$$

$$\frac{d}{dt}\int_V |\psi(\overrightarrow{r},t)|^2 dV = 0 \tag{3.48}$$

$$\int_V \dot{\psi}^*\psi + \psi^*\dot{\psi} dV = 0 \tag{3.49}$$

$$\int_V \frac{1}{i\hbar}\left[-(H\psi)^*\psi + \psi^* H\psi\right] dV = 0 \tag{3.50}$$

$$\frac{1}{i\hbar}\int_V -\left[-\frac{\hbar^2}{2m}\triangle + V(\overrightarrow{r},t)\right]\psi^*\psi +$$

$$\psi^*\left[-\frac{\hbar^2}{2m}\triangle + V(\overrightarrow{r},t)\right]\psi dV = 0 \tag{3.51}$$

$$\frac{1}{i\hbar}\int_V \frac{\hbar^2}{2m}\left[\psi\triangle\psi^* - \psi^*\triangle\psi\right] dV = 0 \tag{3.52}$$

$$\frac{i\hbar}{2m}\int_V \left[\psi^*\triangle\psi - \psi\triangle\psi^*\right] dV = 0 \tag{3.53}$$

$$\frac{i\hbar}{2m}\int_V \overrightarrow{\nabla}\bullet\left[\psi^*\overrightarrow{\nabla}\psi - \psi\overrightarrow{\nabla}\psi^*\right] dV = 0 \tag{3.54}$$

$$\text{with Gauss} \quad \int_V \overrightarrow{\nabla}\bullet\overrightarrow{E}(\overrightarrow{r})dV = \oint_{\partial V}\overrightarrow{E}(\overrightarrow{r})\bullet d\overrightarrow{f} \tag{3.55}$$

$$\text{and Stokes} \int_{\partial F}\overrightarrow{A}(\overrightarrow{r})\bullet d\overrightarrow{r} = \int_F \overrightarrow{\nabla}\times d\overrightarrow{f} \tag{3.56}$$

$$\oint_{\partial V}\frac{i\hbar}{2m}\left[\psi^*\overrightarrow{\nabla}\psi - \psi\overrightarrow{\nabla}\psi^*\right]\bullet d\overrightarrow{f} = 0 \tag{3.57}$$

$$\oint_{\partial V}\overrightarrow{j}(\overrightarrow{r},t)\bullet d\overrightarrow{f} = 0 \tag{3.58}$$

$$\frac{i\hbar}{2m}\left[\psi^*\overrightarrow{\nabla}\psi - \psi\overrightarrow{\nabla}\psi^*\right] = \overrightarrow{j}(\overrightarrow{r},t) \tag{3.59}$$

$$\Rightarrow \frac{\partial\varrho}{\partial t} + \overrightarrow{\nabla}\bullet\overrightarrow{(}j) = 0 \tag{3.60}$$

Equation (3.60) is the continuity equation, describing that the change in density ϱ is given by the loss of probability density $\overrightarrow{j}$.

As mentioned before the expectation value of an operator $\overrightarrow{r}$, given by $\langle\overrightarrow{r}\rangle$ or $\langle\widetilde{\overrightarrow{r}}\rangle$ is an observable, which can be measured in experiments. The uncertainty of an observable κ is given by its variance (or second weight) $\Delta\kappa$:

$$\Delta\kappa = \sqrt{\langle\kappa^2\rangle - \langle\kappa\rangle^2} \tag{3.61}$$

It is easy to show that for a hermitian operator A

$$\begin{aligned}
\Delta A &\equiv \sqrt{\langle\psi|A^2\psi\rangle - \langle\psi|A\psi\rangle^2} \geq 0 && (3.62)\\
(\Delta A)^2 &= \langle\psi|(A - \langle A\rangle)^2\psi\rangle && (3.63)\\
&= \langle\psi|(A^2 - 2A\langle A\rangle + \langle A\rangle^2)\psi\rangle && (3.64)\\
&= \langle\psi|A^2\psi\rangle - 2\langle A\rangle\langle A\rangle + \langle A\rangle^2 && (3.65)\\
&= \langle\psi|A^2\psi\rangle - \langle\psi|A\psi\rangle^2 && (3.66)\\
&= \langle(A - \langle A\rangle)\psi|(A - \langle A\rangle)\psi\rangle = \|(A - \langle A\rangle\|^2 \geq 0. && (3.67)
\end{aligned}$$

the variance is always positive and zero if ψ is eigenfunction of A and $A\psi = a\psi$ and therefore $\langle A\rangle = a$.

Commutators are defined by

$$[A, B] \equiv AB - BA \tag{3.68}$$

and if $[A, B] = 0$ the commutators commute, they are independent of each other, and have the same eigenfunctions. For the variance of two operators A and B the following holds:

$$(\Delta A)(\Delta B) \geq \frac{1}{2}|\langle\varphi|[A, B]\varphi\rangle| \tag{3.69}$$

To proof equation (3.69) we introduce two operators A' and B' with

$$\begin{aligned}
A' &\equiv A - \langle\varphi|A\varphi\rangle && (3.70)\\
B' &\equiv B - \langle\varphi|B\varphi\rangle && (3.71)\\
\Rightarrow \langle\varphi|A'\varphi\rangle &= \langle\varphi|(A - \langle A\rangle)\varphi\rangle && (3.72)\\
&= \langle A\rangle - \langle A\rangle && (3.73)\\
\langle\varphi|A'\varphi\rangle &= 0 && (3.74)\\
\langle\varphi|B'\varphi\rangle &= 0 && (3.75)
\end{aligned}$$

The variance and commutator of A' and B', which are hermitian has the following properties:

$$
\begin{aligned}
[A', B'] &= [A, B] && (3.76)\\
(\Delta A')^2 &\overset{\langle A'\rangle=0}{=} \langle\varphi|(A')^2\varphi\rangle && (3.77)\\
&= \langle\varphi|(A - \langle A\rangle)^2\varphi\rangle && (3.78)\\
&= (\Delta A)^2 && (3.79)\\
(\Delta B')^2 &= (\Delta B)^2 && (3.80)
\end{aligned}
$$

With this one can show the general uncertainty relation:

$$
\begin{aligned}
(\Delta A')^2(\Delta B')^2 &= \langle\varphi|(A')^2\varphi\rangle\langle\varphi|(B')^2\varphi\rangle && (3.81)\\
&= \|A'\varphi\|^2\|B'\varphi\|^2 && (3.82)\\
&\geq |laA'\varphi|B'\varphi\rangle|^2 && (3.83)\\
&\geq |\Im(\langle A'\varphi|B'\varphi\rangle)|^2 && (3.84)\\
&= |\frac{1}{2i}(\langle A'\varphi|B'\varphi\rangle - \langle A'\varphi|B'\varphi\rangle^*)|^2 && (3.85)\\
&= \frac{1}{4}|(\langle\varphi|A'B'\varphi\rangle - \langle B'A'\varphi|\varphi\rangle^*)|^2 && (3.86)\\
&= \frac{1}{4}|(\langle\varphi|A'B'\varphi\rangle - \langle\varphi|B'A'\varphi\rangle)|^2 && (3.87)\\
&= \frac{1}{4}|\langle\varphi|[A', B']\varphi\rangle|^2 && (3.88)\\
&= \frac{1}{4}|\langle\varphi|[A, B]\varphi\rangle|^2 && (3.89)\\
\Rightarrow (\Delta A')^2(\Delta B')^2 &\geq \frac{1}{4}|\langle\varphi|[A, B]\varphi\rangle|^2 && (3.90)\\
\Rightarrow (\Delta A')(\Delta B') &\geq \frac{1}{2}|\langle\varphi|[A, B]\varphi\rangle| && (3.91)
\end{aligned}
$$

For the example of the space operator $\overrightarrow{r}$ and the momentum operator $\overrightarrow{p} = \frac{\hbar}{i}\overrightarrow{\nabla}$ equation (3.69) becomes:

$$
\begin{aligned}
[\overrightarrow{r}, \overrightarrow{p}]_i\Phi &= [\overrightarrow{r}, \frac{\hbar}{i}\overrightarrow{\nabla}]_i\Phi && (3.92)\\
&= \frac{\hbar}{i}(\overrightarrow{r}\overrightarrow{\nabla} - \overrightarrow{\nabla}\overrightarrow{r})_i\Phi && (3.93)\\
&= \frac{\hbar}{i}(\overrightarrow{r_i}\overrightarrow{\nabla_i}\Phi - \overrightarrow{r_i}\overrightarrow{\nabla_i}\Phi - \Phi\overrightarrow{\nabla_i}\overrightarrow{r_i}) && (3.94)\\
&= -\frac{\hbar}{i}\Phi\mathbf{r_i} && (3.95)\\
\Rightarrow [\overrightarrow{p}, \overrightarrow{r}]_i &= \frac{\hbar}{i} && (3.96)\\
\Rightarrow \Delta\overrightarrow{p_i}\Delta\overrightarrow{r_i} &\geq \frac{\hbar}{2} && (3.97)
\end{aligned}
$$

So we see that it is impossible to measure the exact location and momentum of a particle at the same time.

4 Particle in a box

Assume the most simplest way of localizing a particle in a one-dimensional (x-axis) box of length 2a, with boundary conditions, so that the potential jumps at the positions $x = -a$ and $x = a$ from zero to infinite (Fig. 4).

$$V(x) = \left\{ \begin{array}{ccc} 0 & , & |x| < a \\ \infty & , & else \end{array} \right\} \tag{4.1}$$

Since at space positions $|x| \geq a$ the potential is infinite, the probability of the

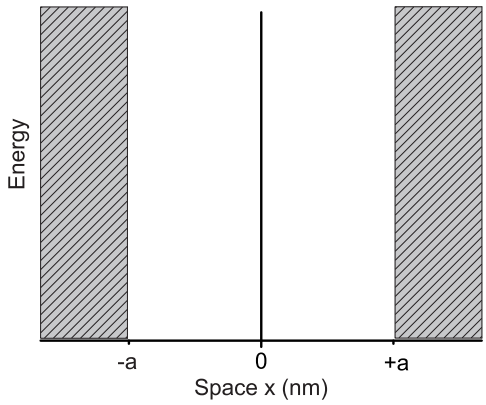


Abbildung 4.1. Potential function V(x) for a particle in a box.

wave function has to vanish for those positions, i.e. the particle is trapped between the potential walls. This leads us to the boundary conditions

$$\Psi(a) = \Psi(-a) = 0 \tag{4.2}$$

of the SE for a particle in a box with $V(x) = 0$ inside of the box:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x) = E\Psi(x) \tag{4.3}$$

This is the SE of a free particle with symmetric and periodic boundary conditions. We can try to solve the SE equation with the following wave functions:

$$\begin{aligned}
\Psi_g &= \cos(k_n x) && (4.4)\\
\Rightarrow \frac{\hbar^2 k^2}{2m}\Psi_g &= E\Psi_g && (4.5)\\
\Psi_g(a) &= \cos(k_n a) = 0 && (4.6)\\
\Psi_g(-a) &= \cos(k_n a) = 0 && (4.7)\\
\Rightarrow k_n a &= n\frac{\pi}{2}, \quad n \text{ odd} && (4.8)\\
\Psi_u &= \sin(k_n x) && (4.9)\\
\Psi_u(a) &= \sin(k_n a) = 0 && (4.10)\\
\Psi_u(-a) &= -\sin(k_n a) = 0 && (4.11)\\
\Rightarrow k_n a &= n\frac{\pi}{2}, \quad n \text{ even} && (4.12)\\
\Rightarrow k_n &= \frac{n\pi}{2a} && (4.13)\\
\Rightarrow E_n &= \frac{\hbar^2 k_n^2}{2m} = \frac{\pi^2\hbar^2 n^2}{8ma^2}, \quad \text{n} = 1, 2, \ldots && (4.14)
\end{aligned}$$

The solutions of the wave functions for the particle in a box and the energies have the following properties:

- discrete eigenvalues for the energy E_n (discrete energy spectrum)
- $E_n \propto n^2$ and $E_n \propto a^{-2}$
- the lowest energy is $E_1 = \frac{\pi^2\hbar^2}{8ma^2}$ and not zero
- with increasing n, Ψ_n the number of nodes increases (n-1)
- the stationary states are either even $\{\cos(k_n x)\}$ or odd $\{\sin(k_n x)\}$. This follows from the parity symmetry $V(x) = V(-x)$.
- The eigenfunctions are orthogonal and complete $\langle\Psi_n|\Psi_m\rangle = \kappa\delta_{n,m}$.
- the normalization c_n has to be chosen such as $\int_{-a}^{a} c_n^2 \cos^2(\frac{n\pi x}{2a})dx = 1$
- the position expectation value is zero $\langle x\rangle = 0$
- the momentum expectation value is zero $\langle p_x\rangle = 0 = \int_{-a}^{a} \sin(\frac{n\pi x}{2a})\frac{\hbar}{i}\frac{d}{dx}\sin(\frac{n\pi x}{2a})dx$
- in a classical picture the probability $P(x)$ would be equal for every space position $P(x) = \frac{1}{2a}$, whereas the quantum mechanical description exhibits positions where the probability is zero (nodes) and positions where the probability is higher.

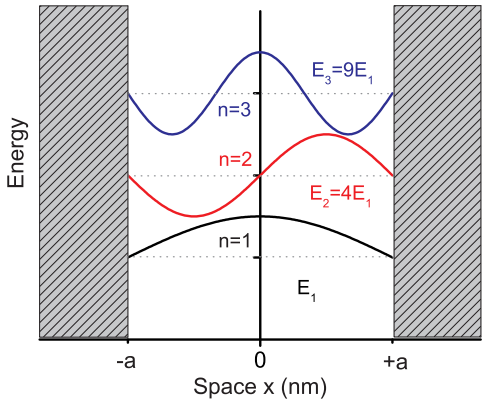


Abbildung 4.2. Wave functions Ψ_n with $n = 1, 2, 3$ of a particle in a box with energies $E_1 = \frac{\pi^2\hbar^2}{8ma^2}$, E_2, and E_3.

5 Ground state of the hydrogen atom

To test whether the SE gives reasonable answers to physical problems we calculate the ground state of a hydrogen atom, which is experimentally well characterized. The potential operator of the hydrogen atom $V(\overrightarrow{r}) = V(r)$ has radial symmetry, so that the eigenfunction in the lowest ground state should depend only on r. With this assumption the part in the $\triangle$ operator depending on ϕ and θ can be neglected. The eigenfunction corresponding to the lowest energy E_1 is $\varphi_1(r)$ and it should solve the SE:

$$\left[-\frac{\hbar^2}{2m}\triangle + V(r)\right]\varphi_1(r) = E_1\varphi_1(r) \tag{5.1}$$

$$\left[-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right) + V(r)\right]\varphi_1(r) = E_1\varphi_1(r) \tag{5.2}$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\varphi_1(r) - \frac{Ze^2}{4\pi\epsilon_0 r}\varphi_1(r) = E_1\varphi_1(r) \tag{5.3}$$

If we try now the wave function $\varphi_1(r) \propto e^{-r/a}$, which is square integrable, we get:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{a^2} - \frac{2}{ra}\right]\varphi_1(r) - \frac{Ze^2}{4\pi\epsilon_0 r}\varphi_1(r) = E_1\varphi_1(r) \tag{5.4}$$

The wave function can only be a solution if the $\frac{1}{r}$ terms cancel each other:

$$\frac{2\hbar^2}{2ma} = \frac{Ze^2}{4\pi\epsilon_0} \Rightarrow a = \frac{4\pi\epsilon_0\hbar^2}{Ze^2m} \tag{5.5}$$

With $Z = 1$ this is exactly the Bohr's radius a_0, and the energy E_1 is given by:

$$E_1 = -\frac{\hbar^2}{2ma^2} = -\frac{\hbar^2}{2m}\frac{Z^2e^4m^2}{16\pi^2\epsilon_0^2\hbar^4} = -\frac{Z^2e^4m}{32\pi^2\epsilon_0^2\hbar^2}. \tag{5.6}$$

The energy $E_1 = -13.6\,\text{eV}$ is the same as calculated by Bohr's model. The wave

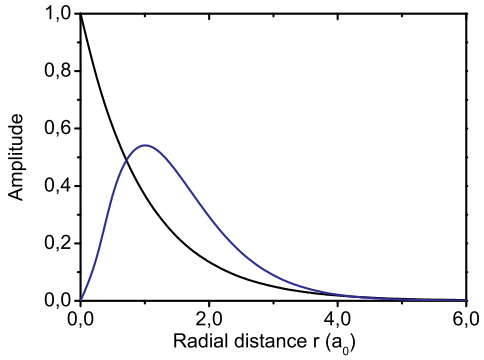


Abbildung 5.1. Wave functions $\varphi_1(r)$ of a hydrogen atom (black) and the probability to find an electron between r and $r + dr$, given by $|\varphi_1(r)|^2 r^2 dr$ (blue).

function is maximal at $r = 0$, but due to the polar coordinates, integration over the volume element $dV = r^2 dr d(\cos\theta) d\varphi$ introduces an additional r^2 dependency, so that the probability of finding the electron at the nucleus is zero (Fig. 5). The probability of finding an electron between r and $r + dr$ is given by

$$P(r, r+dr) \propto |\varphi_1(r)|^2 r^2 dr \propto r^2 e^{-2r/a_0} dr. \tag{5.7}$$

Here, the normalization is missing! To find the maximum of the probability (not the expectation value) we have to differentiate:

$$\frac{d}{dr}(r^2 e^{-\frac{2r}{a_0}}) = 2re^{-\frac{2r}{a_0}} - \frac{2r^2}{a_0} e^{-\frac{2r}{a_0}} = 0 \tag{5.8}$$

$$\Rightarrow 2r - \frac{2r^2}{a_0} = 0 \tag{5.9}$$

$$\Rightarrow r_{max} = a_0 \tag{5.10}$$

The energy value E_1 and the dimension parameters a_0 are still valid, but there is no electron moving, now we have a stationary system with the angular momentum start at zero.

6 General remarks to solve the SE

For one dimensional problems we can write the SE as follows:

$$\frac{d^2\Psi(x)}{dx^2} = \frac{2m}{\hbar^2}(V(x) - E)\Psi(x) \tag{6.1}$$

The sign of $\frac{d^2\Psi(x)}{dx^2}$ determines the curvature of $\Psi(x)$ and is given by $V(x) - E$. In

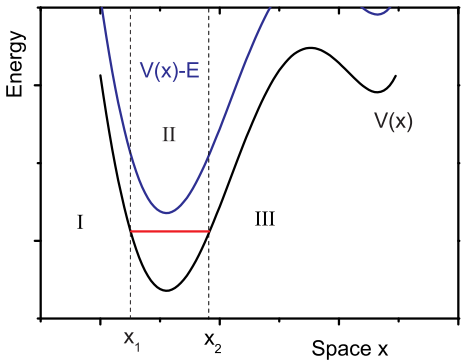


Abbildung 6.1. Arbitrary potential $V(x)$ (black) with a given energy (red) and the difference of $V(x) - E$.

a classical potential $V(x)$ (1-D) the probability of finding the particle between x_1 and x_2 is proportional to $\frac{1}{p} = \frac{1}{\sqrt{2m(E-V(x))}}$ (Fig. 6). It is maximal for the points x_1 and x_2 and minimal for the minimum of $V(x)$. In the space regions of I and III, $\frac{1}{p}$ is imaginary and classically forbidden. For the wave functions the regions I and III are not forbidden (tunneling effect), but there the term $V(x) - E \geq 0$ and the wave function shows exponential character

$$\Psi \propto e^{\pm\kappa x}, \quad \text{with} \quad \kappa = \frac{1}{\hbar}\sqrt{2m(V(x) - E)} \tag{6.2}$$

for slowly varying V(x). In the region II $V(x) - E \leq 0$ and the wave function has oscillatory character.

$$\Psi \propto e^{\pm i\kappa x}, \quad \text{with} \quad \kappa = \frac{1}{\hbar}\sqrt{2m(E - V(x))} \tag{6.3}$$

In region I and III $\frac{d^2\Psi}{x^2}$ has the same sign as Ψ, so that the wave functions shape

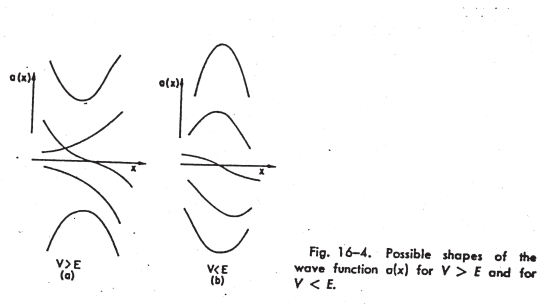


Fig. 16–4. Possible shapes of the wave function a(x) for $V > E$ and for $V < E$.

is concave with respect to the x-axis. In region II $\frac{d^2\Psi}{x^2}$ has the opposite sign as Ψ, so that the wave functions shape is convex with respect to the x-axis (Fig.

6). Convex shapes lead to oscillatory signals. At the positions x_1 and x_2 where $V(x) = E$ the second derivative is zero and the sign changes. This holds also for classical models. Upon introducing the boundary conditions the spectrum becomes discrete with a non zero lowest energy. Discrete energy eigenvalues next to each other have eigenfunctions differing in one node, with Ψ_n has (n-1) nodes. With increasing n the envelope function of $|\Psi_n|^2$ gets more and more similar to the classical probability function $\frac{1}{p}$. As a result of those differences in quantum mechanical versus classical behavior, tunneling effects are possible and in the lowest state the probability is highest in the minimum of the potential.

7 Harmonic oscillator 1-D

The harmonic oscillator is well known from the mechanical spring with spring constant k and oscillation frequency $\omega = \sqrt{\frac{k}{m}}$. With Hook's law $\overrightarrow{F} = -k\overrightarrow{r}$ it is easy to calculate the potential energy and the Hamilton function of a harmonic oscillator to be

$$V(x) = \frac{1}{2}kx^2 \tag{7.1}$$

$$H(x) = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + \frac{1}{2}kx^2\Psi \tag{7.2}$$

$$H\Psi = E\Psi \tag{7.3}$$

We perform a variable transformation

$$y = \sqrt{\frac{m\omega}{\hbar}}x \tag{7.4}$$

$$\lambda = \frac{2E}{\hbar\omega} \tag{7.5}$$

With this transformation the SE becomes

$$\left(\frac{d^2}{dy^2} - y^2\right)\Psi_\lambda = -\lambda\Psi_\lambda \tag{7.6}$$

Now, we calculate the following operators:

$$\left(\frac{d}{dy} + y\right)\left(\frac{d}{dy} - y\right)\Psi_\lambda = \left(\frac{d^2}{dy^2} - y^2 - 1\right)\Psi_\lambda \tag{7.7}$$

$$\left(\frac{d}{dy} - y\right)\left(\frac{d}{dy} + y\right)\Psi_\lambda = \left(\frac{d^2}{dy^2} - y^2 + 1\right)\Psi_\lambda \tag{7.8}$$

and define the lowering operator

$$a = \left(\frac{d}{dy} + y\right) \tag{7.9}$$

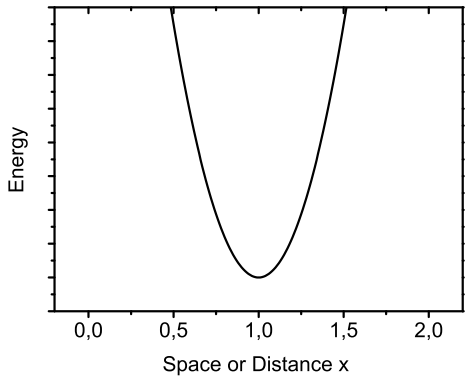


Abbildung 7.1. Potential of an one dimensional harmonic oscillator.

and the rising operator

$$a^+ = \left(\frac{d}{dy} - y\right) \tag{7.10}$$

and inserting (7.9) and (7.10) into equations (7.7)and (7.8) we get

$$\left(\frac{d^2}{dy^2} - y^2\right)\Psi_\lambda = (aa^+ + 1)\Psi_\lambda \tag{7.11}$$

$$\left(\frac{d^2}{dy^2} - y^2\right)\Psi_\lambda = (a^+a - 1)\Psi_\lambda \tag{7.12}$$

and we can write the SE as follows

$$aa^+\Psi_\lambda = -(\lambda + 1)\Psi_\lambda \tag{7.13}$$

$$a^+a\Psi_\lambda = -(\lambda - 1)\Psi_\lambda \tag{7.14}$$

$$(\Rightarrow a^+a - aa^+)\Psi_\lambda = 2\Psi_\lambda, \quad \forall\Psi_\lambda \tag{7.15}$$

$$\Rightarrow a^+a - aa^+ = 2 \tag{7.16}$$

If we take the following equation

$$a^+a(a\Psi_\lambda) = (2 + aa^+)(a\Psi_\lambda) \tag{7.17}$$

$$= 2a\Psi_\lambda + a(a^+a\Psi_\lambda) \tag{7.18}$$

$$= 2a\Psi_\lambda + a(-(\lambda - 1))\Psi_\lambda \tag{7.19}$$

$$= -(\lambda - 3)a\Psi_\lambda \tag{7.20}$$

$$a^+a\Phi = -(\lambda - 3)\Phi \tag{7.21}$$

Thus, the equation for the eigenvalue $(\lambda - 3)$ is given by

$$a^+a\Psi_{\lambda-2} = (\lambda - 3)\Psi_{\lambda-2} \tag{7.22}$$

$$a\Psi_\lambda = \Phi = \Psi_{\lambda-2} \tag{7.23}$$

$$\Rightarrow a\Psi_\lambda = \Psi_{\lambda-2} \tag{7.24}$$

Thus, the eigenfunctions of $\Psi_{\lambda-2}$ can be generated by applying the operator $a = \frac{d}{dy} + y$ on the eigenfunction Ψ_λ. With this process one can calculate the eigenfunctions for eigenvalues of $\lambda-2, \lambda-4, \lambda-6, \ldots$ if we have the eigenfunction Ψ_λ. In addition, this process stops at the minimal eigenvalue of $\lambda = \frac{2E}{\hbar\omega}$, because the energy of the harmonic oscillator is positive, as shown below.

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\Psi_E = E\Psi_E \tag{7.25}$$

$$\Rightarrow \int_{-\infty}^{\infty} \Psi_E^*(x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\Psi_E(x)dx + \tag{7.26}$$

$$\int_{-\infty}^{\infty} \Psi_E^*(x)\left(\frac{1}{2}kx^2\right)\Psi_E(x)dx = E\int_{-\infty}^{\infty}\Psi_E^*(x)\Psi_E(x)dx$$

$$-\frac{\hbar^2}{2m}\Psi_E^*(x)\frac{d\Psi_E(x)}{dx}\Big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty}\frac{d\Psi_E^*(x)}{dx}\frac{d\Psi_E(x)}{dx}dx + \tag{7.27}$$

$$\frac{1}{2}k\int_{-\infty}^{\infty}\Psi_E^*(x)x^2\Psi_E(x)dx = E\int_{-\infty}^{\infty}\Psi_E^*(x)\Psi_E(x)dx$$

In (7.28) the first term is zero, because the wave function has to vanish for $\lim_{x\to\infty}\Psi(x) \to 0$. The second integral $\langle\frac{d\Psi}{dx}|\frac{d\Psi}{dx}\rangle \geq 0$ is positive, because of the properties of the scalar product. The last integral $\langle\Psi|x^2\Psi\rangle = \langle x\Psi|x\Psi\rangle \geq 0$ is also positive, so that the energy has to be fulfil $E \geq 0$. The energy is zero only for the trivial solution $\Psi(x) \equiv 0$. So we can conclude that there exists a minimal value for λ

$$\exists\lambda_M \tag{7.28}$$

$$a\Psi_{\lambda_M} = 0 \tag{7.29}$$

$$a^+a\Psi_{\lambda_M} = -(\lambda_M - 1)\Psi_{\lambda_M} \tag{7.30}$$

$$= a^+0 = 0 \tag{7.31}$$

$$\overset{\Psi_{\lambda_M}\neq 0}{\Rightarrow} \lambda_M = 1 \tag{7.32}$$

So the spectrum of the eigenvalues is given by

$$\lambda = \{1, 3, 5, 7, \ldots\} = 2n + 1, \quad n = \{0, 1, 2, \ldots\} \tag{7.33}$$

and the eigenvalues of the energies are calculated to be

$$\lambda = \frac{2E}{\hbar\omega}$$

$$E_n = (2n+1)\frac{\hbar\omega}{2} = (n + \frac{1}{2})\hbar\omega, \quad n = 0, 1, 2, \ldots \tag{7.34}$$

We determined the eigenvalues for the harmonic oscillator without knowing the eigenfunctions.

In order to determine the eigenfunctions of the harmonic oscillator we make use of the properties of the a^+ operator

$$a^+\Psi_\lambda \propto \Psi_{\lambda+2} \tag{7.35}$$
$$a^+\Psi_n \propto \Psi_{n+1}. \tag{7.36}$$

If we have identified Ψ_0 we can calculate Ψ_n iteratively, using

$$\Psi_n \propto (a^+)^n\Psi_0 \propto \underbrace{\left(\frac{d}{dy}-y\right)\cdots\left(\frac{d}{dy}-y\right)}_{\text{n factors}}\Psi_0. \tag{7.37}$$

The first eigenfunction Ψ_0 we can determine as follows

$$a\Psi_0 = 0 \tag{7.38}$$
$$\left(\frac{d}{dy}+y\right)\Psi_0 = 0 \tag{7.39}$$
$$\Rightarrow \frac{d\Psi_0}{\Psi_0} = -ydy \tag{7.40}$$
$$\Rightarrow \Psi_0 = N_0 e^{-\frac{y^2}{2}}. \tag{7.41}$$

Here, N_0 is the normalization constant to guarantee that $\langle\Psi_0|\Psi_0\rangle = 1$. The function Ψ_0 is clearly square integrable. Now, we can derive the Ψ_n

$$\Psi_1 \propto a^+\Psi_0 \propto 2ye^{-\frac{y^2}{2}} \tag{7.42}$$
$$\Psi_2 \propto (a^+)^2\Psi_0 \propto (4y^2-2)e^{-\frac{y^2}{2}} \tag{7.43}$$

The eigenfunctions Ψ_n are products of a gaussian type of function $e^{-\frac{y^2}{2}}$ with a Hermite polynomial. The gaussian function is even with respect to y and the Hermite polynomial is either even or odd, so that the eigenfunctions are also even or odd. This is a direct consequence of the potentials symmetry $V(-x) = V(x)$. The general description to derive Hermite polynomials is given by

$$H_n(y) = \frac{(-1)^n}{\sqrt{2^n n!\sqrt{\pi}}}\ e^{y^2}\left(\frac{d^n}{dy^n}\right)e^{-y^2} \tag{7.44}$$

We can determine the unknown factor by make use of the normalization condition

$$\int_{-\infty}^{\infty} e^{-y^2}H_n^2(y)dy = 1 \tag{7.45}$$

If we transform y back we get $\Psi_n(x)$

$$\Psi_n(x) = \sqrt[4]{\frac{m\omega}{\hbar}} e^{-\frac{m\omega x^2}{2\hbar}} H_n(x\sqrt{\frac{m\omega}{\hbar}}) \tag{7.46}$$

As a result the eigenfunction $\Psi_0(x)$ of the lowest energy eigenvalue $E_0 = \frac{\hbar\omega}{2}$ has the following form

$$\Psi_0(x) = \sqrt[4]{\frac{m\omega}{\hbar}} e^{-\frac{m\omega x^2}{2\hbar}}. \tag{7.47}$$

This is a gaussian function with the maximum of $|\Psi_0(x)|^2$ at $x = 0$. At this point the space probability density is highest. In a classical picture the space probability density would be minimal at $x = 0$. Hermite polynomials

$$H_n(y)\sqrt{2^n n!\sqrt{\pi}} = \widehat{H}_n(y) = (-1)^n e^{y^2} \left(\frac{d^n}{dy^n}\right) e^{-y^2} \tag{7.48}$$

$$\widehat{H}_0(y) = 1 \tag{7.49}$$

$$\widehat{H}_1(y) = 2y \tag{7.50}$$

$$\widehat{H}_2(y) = 4y^2 - 2 \tag{7.51}$$

$$\widehat{H}_3(y) = 8y^3 - 12y \tag{7.52}$$

$$\widehat{H}_4(y) = 16y^4 - 48y^2 + 12 \tag{7.53}$$

$$\widehat{H}_5(y) = 32y^5 - 160y^3 + 120y \tag{7.54}$$

$$\widehat{H}_6(y) = 64y^6 - 480y^4 + 720y^2 - 120 \tag{7.55}$$

$$\widehat{H}_7(y) = 128y^7 - 1344y^5 + 3360y^3 - 1680y \tag{7.56}$$

$$\widehat{H}_8(y) = 256y^8 - 3584y^6 + 13440y^4 - 13440y^2 + 1680 \tag{7.57}$$

The Hermite polynomials have the following properties:

$$\ddot{H}_n - 2y\dot{H}_n + 2nH_n = 0 \tag{7.58}$$

$$2yH_n - 2nH_{n-1} = H_{n+1} \tag{7.59}$$

$$\int_{-\infty}^{\infty} H_n(y)H_m(y)e^{y^2}dy = \delta_{n,m} \tag{7.60}$$

Using equation (7.58) we obtain for $a^+a\Psi_n$ the equation

$$
\begin{aligned}
a^+a\Psi_n &= \left(\frac{d^2}{dy^2} - y^2 + 1\right) H_n e^{-y^2/2} && (7.61)\\
&= \frac{d^2}{dy^2} H_n e^{-y^2/2} - y^2 H_n e^{-y^2/2} + H_n e^{-y^2/2}\\
&= \frac{d}{dy}\left(\dot{H}_n e^{-y^2/2} - y H_n e^{-y^2/2}\right) - y^2 H_n e^{-y^2/2} + H_n e^{-y^2/2}\\
&= \left(\ddot{H}_n e^{-y^2/2} - y\dot{H}_n e^{-y^2/2} - y\dot{H}_n e^{-y^2/2} - H_n e^{-y^2/2} + y^2 H_n e^{-y^2/2}\right)\\
&\quad -y^2 H_n e^{-y^2/2} + H_n e^{-y^2/2}\\
&= \ddot{H}_n e^{-y^2/2} - 2y\dot{H}_n e^{-y^2/2}\\
&= -2nH_n && (7.62)
\end{aligned}
$$

For further information see M.Abramowitz and I.A. Stegun, *Handbook of mathematical functions*, Dover (1965), Chapter 22. The solutions of the wave functions for a particle in a box and for the harmonic oscillator (Fig. 7) have some similarities:

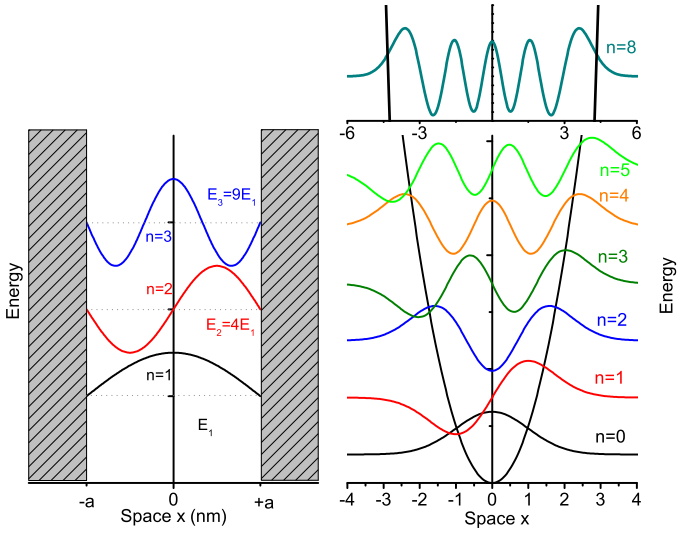


Abbildung 7.2. Comparison of wave functions of the particle in a box and the harmonic oscillator.

- Discrete solutions and eigenenergies.
- The n th wave function has n nodes.

- The lowest energy has a finite positive value $E_0 = \frac{\hbar\omega}{2} \geq 0$. Result of the uncertainty relation.
- The eigenfunctions of different eigenvalues are orthogonal. General property of the Hamilton operator.

7.1 Conserved quantities

In general physical quantities, which can be measured, give real values and are therefore related to hermitian operators:

$$\left(\int \Phi^* A \Phi dV\right)^* = \int \Phi^* A \Phi dV \tag{7.63}$$

- Operator hermitian
- Eigenfunctions orthonormal $A\Phi_n = a\Phi_n$. For degenerate energies the eigenfunctions can be chosen as orthonormal. $\int \Psi_m^* \Psi_n dV = \delta_{mn}$.
- The eigenfunctions form a complete set of orthonormal functions if every function of the space can be developed as $\Psi(\overrightarrow{r}) \sum_n c_n \psi_n(\overrightarrow{r})$.

The closure relation (7.69)follows from the complete set of the eigenfunctions $\psi_n(\overrightarrow{r})$

$$\begin{aligned}
\Psi(\overrightarrow{r}) &= \sum_n c_n \psi_n(\overrightarrow{r}) && (7.64)\\
\langle \psi_m(\overrightarrow{r}) | \Psi(\overrightarrow{r}) \rangle &= \sum_n c_n \langle \psi_m(\overrightarrow{r}) | \psi_n(\overrightarrow{r}) \rangle && (7.65)\\
&= \sum_n c_n \delta_{m,n} = c_{m=n} && (7.66)\\
\Rightarrow \Psi(\overrightarrow{r}) &\stackrel{!}{=} \sum_k \langle \psi_k(\overrightarrow{r'}) | \Psi(\overrightarrow{r'}) \rangle \psi_k(\overrightarrow{r}) && (7.67)\\
&= \sum_k \int \psi_k^*(\overrightarrow{r'}) \psi_k(\overrightarrow{r}) \Psi(\overrightarrow{r'}) d\overrightarrow{r'} && (7.68)\\
\Rightarrow \sum_k \psi_k(\overrightarrow{r'}) \psi_k(\overrightarrow{r}) &= \delta(\overrightarrow{r} - \overrightarrow{r'}) && (7.69)
\end{aligned}$$

A very important issue in physics is the identification of conserved quantities. Since we are interested in expectation values of a given operator u, the time dependence of $\langle u \rangle$ is given by:

$$\frac{d\langle u \rangle}{dt} = \frac{1}{i\hbar} \langle [u, H] \rangle + \langle \frac{\partial u}{\partial t} \rangle \tag{7.70}$$

If $\frac{du}{dt} = 0$ then $\langle u \rangle$ is conserved, and it is a conserved quantity if u and H commute:

$$[u, H] = 0 \tag{7.71}$$

Especially, if at time $t = 0$ the system is in an eigenstate of u with eigenvalue u_i, the system will stay in that state. The subscript i of the eigenvalue u_i is called good quantum number, because it is a conserved quantity and describes the quantum system. The eigenvalues u_i are possible observable quantities. If we want to indicate that the eigenfunctions of the energy E_n are at the same time eigenfunctions of the operator u with eigenvalue u_m, we have to introduce two indices:

$$H\Psi_{n,m} = E_n\Psi_{n,m} \tag{7.72}$$
$$u\Psi_{n,m} = u_m\Psi_{n,m} \tag{7.73}$$

On the other hand, if there are eigenfunctions $\Psi_{n,m}$ of u and H, then it follows:

$$uH\Psi_{n,m} = uE_n\Psi_{n,m} = E_nu\Psi_{n,m} = E_nu_m\Psi_{n,m} \tag{7.74}$$
$$Hu\Psi_{n,m} = Hu_m\Psi_{n,m} = u_mH\Psi_{n,m} = u_mE_n\Psi_{n,m} \tag{7.75}$$
$$\Rightarrow (uH - Hu)\Psi_{n,m} = 0 \tag{7.76}$$
$$\Rightarrow [u, H] = 0 \tag{7.77}$$

If equation (7.77) is given it is easy to show that there are eigenfunctions $\Psi_{n,m}$ of u and H.

The same holds for every set of operators A_i. If $[A_i, A_j] = 0$ then A_i and A_j have the same eigenfunctions. If additionally, $[A_i, H] = 0$ holds, and therefore $\langle A_i \rangle$ is constant, the operator A_i has the same eigenfunctions as the energy operator. To characterize the energy eigenfunctions in the best possible way, we are looking for the maximal set of operators A_j, which commute with the Hamilton operator and with themselves:

$$[A_i, A_j] = 0, \quad \forall i, j \tag{7.78}$$
$$[A_i, H] = 0, \quad \forall i \tag{7.79}$$

That means there are eigenfunctions of H, A_1, $A_2, \ldots$ at the same time and the quantum numbers of those operators are good quantum numbers describing the system.

A system with a potential $V(\overrightarrow{r}) = V(r)$ only dependent on the length of the radius $|\overrightarrow{r}|$, such as the hydrogen atom, there are three pairwise commuting operators describing the system:

$$H, \quad \overrightarrow{L}^2, \quad \text{and} \quad L_z \tag{7.80}$$

Thus, $\langle \overrightarrow{L}^2 \rangle$ and $\langle L_z \rangle$ are conserved and there are simultaneous eigenfunctions of H, $\overrightarrow{L}^2$ and L_z. The indices or quantum numbers are n, l, and $\mathrm{m_l}$, and the eigenfunctions are described as

$$\begin{aligned} \Psi_{n,l,m_l} & & (7.81)\\ H\Psi_{n,l,m_l} &= E_n\Psi_{n,l,m_l} & (7.82)\\ \overrightarrow{L}^2\Psi_{n,l,m_l} &= l(l+1)\hbar^2\Psi_{n,l,m_l} & (7.83)\\ L_z\Psi_{n,l,m_l} &= m\hbar\Psi_{n,l,m_l} & (7.84) \end{aligned}$$

7.2 Variational method

The variational method is a very useful method to calculate or approximate wave functions by minimizing parameters and the energy of the system. This technique is especially useful for LCAO (Linear Combination of Atomic Orbitals) methods in molecules. Assume we have to solve the eigenvalue equation

$$\begin{aligned} H\Psi_n &= E_n\Psi_n \quad \text{multiply with } \Psi_n^*, \text{ and integrate :}\\ \Rightarrow E_n &= \frac{\int \Psi_n^* H \Psi_n d\overrightarrow{r}}{\int \Psi_n^* \Psi_n d\overrightarrow{r}} \end{aligned} \tag{7.85}$$

We get the energy eigenvalues if we know the eigenfunctions, but what can we do, if they are unknown? We can start to solve the equation by using a test or trial wave function ψ_{tr}:

$$\epsilon = \frac{\int \psi_{tr}^* H \psi_{tr} d\overrightarrow{r}}{\int \psi_{tr}^* \psi_{tr} d\overrightarrow{r}}. \tag{7.86}$$

For every solution it is $\epsilon \geq E_0$, with E_0 is the lowest energy eigenvalue of the system. To prove that we make use of the complete set and write the trial wave

function as a sum of the orthonormal wave functions of the system:

$$\psi_{tr}(\overrightarrow{r}) = \sum_n c_n \Psi_n(\overrightarrow{r}) \tag{7.87}$$

$$\Rightarrow \int \psi_{tr}^*(H-E_0)\psi_{tr}dV = \sum_n \sum_{n'} c_n^* c_{n'} \int \Psi_n^*(H-E_0)\Psi_{n'}dV \tag{7.88}$$

$$= \sum_n \sum_{n'} c_n^* c_{n'}(E_{n'}-E_0) \int \Psi_n^* \Psi_{n'}dV \tag{7.89}$$

$$= \sum_n \sum_{n'} c_n^* c_{n'}(E_{n'}-E_0)\delta_{nn'} \tag{7.90}$$

$$= \sum_n |c_n|^2(E_n-E_0) \geq 0 \tag{7.91}$$

$$\Rightarrow \int \psi_{tr}^*(H-E_0)\psi_{tr}dV \geq 0, \quad \langle H-E_0\rangle = 0 \text{ if } \psi_{tr}=\Psi_0 \tag{7.92}$$

$$\epsilon = \frac{\int \psi_{tr}^* H \psi_{tr} d\overrightarrow{r}}{\int \psi_{tr}^* \psi_{tr} d\overrightarrow{r}} \geq E_0 \tag{7.93}$$

In order to use this variational method one chooses a trial function ψ_{tr} depending on several parameters $\{a, b, \ldots\}$ and minimize the energy

$$\epsilon(a,b,\ldots), \quad \frac{\partial \epsilon}{\partial a}=0, \frac{\partial \epsilon}{\partial b}=0, \ldots \tag{7.94}$$

for these parameters. This gives the lowest upper limit of E_0 for wave functions of type $\psi_{tr}(a,b,\ldots)$. With a well chosen eigenfunction it is possible to come very close to E_0. As an example one can chose the trial function

$$\psi_{tr} = e^{-\alpha r}, \quad \frac{\partial \epsilon}{\partial \alpha}=0 \tag{7.95}$$

as a test wave function for the hydrogen atom. Upon optimizing the parameter α, it becomes the reciprocal of Bohr's radius $\alpha = \frac{1}{a_0}$ and the energy $\epsilon = E_0$ is exactly the eigenvalue of the hydrogen atom. Here, we get the exact wave solution.

7.3 Angular momentum and spherical potentials

The angular momentum is classically and quantum mechanically defined by:

$$\overrightarrow{L} = \overrightarrow{r} \times \overrightarrow{p} = \begin{vmatrix} \mathbf{e_x} & \mathbf{e_y} & \mathbf{e_z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \tag{7.96}$$

$$\overrightarrow{L} = \frac{\hbar}{i} \begin{vmatrix} \mathbf{e_x} & \mathbf{e_y} & \mathbf{e_z} \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix} \tag{7.97}$$

That means

$$L_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{7.98}$$

$$L_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{7.99}$$

$$L_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{7.100}$$

The components of $\overrightarrow{L}$ are hermitian, but they do **not commute**.

$$[L_x, L_y]\psi = \left(\frac{\hbar}{i}\right)^2 \left\{\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) - \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right\}\psi \tag{7.101}$$

$$= \left(\frac{\hbar}{i}\right)^2 \left\{y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial z \partial x} - yx\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial y \partial x} + zx\frac{\partial^2}{\partial y \partial z} - zy\frac{\partial^2}{\partial x \partial z} + z^2\frac{\partial^2}{\partial x \partial y} + xy\frac{\partial^2}{\partial z^2} - x\frac{\partial}{\partial y} - xz\frac{\partial^2}{\partial z \partial y}\right\}\psi \tag{7.102}$$

$$= \frac{\hbar}{i}\frac{\hbar}{i}\left\{y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right\}\psi = -\frac{\hbar}{i}L_z\psi = i\hbar L_z\psi \quad \forall\psi \tag{7.103}$$

Similar calculations can be performed for the other coordinates, leading to

$$[L_x, L_y] = i\hbar L_z \tag{7.104}$$

$$[L_y, L_z] = i\hbar L_x \tag{7.105}$$

$$[L_z, L_x] = i\hbar L_y \tag{7.106}$$

$$[L_i, L_j] = i\hbar L_k \quad \text{with} \{i, j, k\} \text{ cyclic permutations} \tag{7.107}$$

The hermitian operators L_x, L_y, and L_z are called the angular momentum operators. Since, they do not commutate, there is no common eigenfunction of these operators, but a single component L_i commutes with the operator $\overrightarrow{L}^2$. For con-

venience purposes, we chose the operator L_z to describe the systems properties:

$$\left[L_z, \overrightarrow{L}^2\right] = [L_z, L_x^2 + L_y^2 + L_z^2] = [L_z, L_x^2] + [L_z, L_y^2] \tag{7.108}$$

$$= L_z L_x^2 - L_x^2 L_z + L_z L_y^2 - L_y^2 L_z \tag{7.109}$$

$$= (L_z L_x) L_x - L_x (L_x L_z) - L_y (L_y L_z) + (L_z L_y) L_y \tag{7.110}$$

$$= \underbrace{\underline{L_x (L_z L_x)} - L_x (L_x L_z)}_{1} + \underbrace{(L_z L_x) L_x - \underline{(L_x L_z) L_x}}_{2}$$

$$+ \underbrace{\underline{L_y (L_z L_y)} - L_y (L_y L_z)}_{3} + \underbrace{(L_z L_y) L_y - \underline{(L_y L_z) L_y}}_{4} \tag{7.111}$$

$$= \underbrace{L_x [L_z, L_x]}_{1} + \underbrace{[L_z, L_x] L_x}_{2} + \underbrace{L_y [L_z, L_y]}_{3} + \underbrace{[L_z, L_y] L_y}_{4} \tag{7.112}$$

$$= i\hbar L_x L_y + i\hbar L_y L_x - i\hbar L_y L_x - i\hbar L_x L_y = 0 \tag{7.113}$$

This can be shown faster by using commutator properties. The operator $\overrightarrow{L}^2$ and L_z share the same eigenfunctions. The raising and lowering operators L_+ and L_-, respectively, are rather useful and defined as

$$L_+ = L_x + iL_y \tag{7.114}$$

$$L_- = L_x - iL_y \tag{7.115}$$

$$L_+ L_- = (L_x + iL_y)(L_x - iL_y) = L_x^2 + L_y^2 - i[L_x, L_y] \tag{7.116}$$

$$= \overrightarrow{L}^2 - L_z^2 + \hbar L_z \tag{7.117}$$

$$\overrightarrow{L}^2 = L_+ L_- + L_z^2 - \hbar L_z \tag{7.118}$$

$$\overrightarrow{L}^2 = L_- L_+ + L_z^2 + \hbar L_z \tag{7.119}$$

$$[L_\pm, L_z] = \mp\hbar L_\pm \tag{7.120}$$

$$[L_+, L_-] = 2\hbar L_z \tag{7.121}$$

Now, we have to prove that

$$[H, \overrightarrow{L}^2] = [H, L_z] = 0 \tag{7.122}$$

and the operators H, $\overrightarrow{L}^2$, and L_z share the same eigenfunctions, for $V(\overrightarrow{r}) = V(r)$. To show that we first introduce spherical coordinates and transform the operators to spherical coordinates r, ϑ, φ with the transformation:

$$x = r \sin\vartheta \cos\varphi \tag{7.123}$$

$$y = r \sin\vartheta \sin\varphi \tag{7.124}$$

$$z = r \cos\vartheta \tag{7.125}$$

The derivatives in spherical coordinates are given by

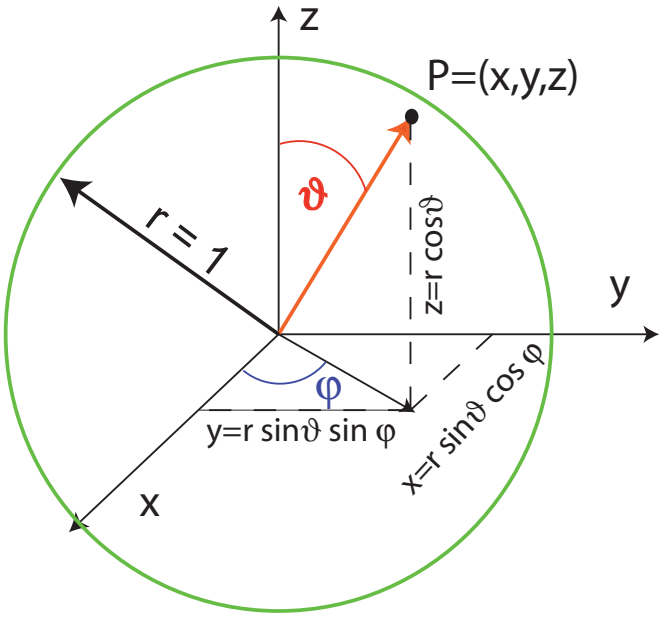


Abbildung 7.3. Spherical coordinates r, ϑ, φ. The coordinates can take the following values: $r \in [0, \infty)$, $\vartheta \in [-\pi, \pi]$, $\varphi \in [0, 2\pi)$.

$$\frac{\partial}{\partial x_i} = \left(\frac{\partial r}{\partial x_i}\frac{\partial}{\partial r}\right) + \left(\frac{\partial \vartheta}{\partial x_i}\frac{\partial}{\partial \vartheta}\right) + \left(\frac{\partial \varphi}{\partial x_i}\frac{\partial}{\partial \varphi}\right), \quad \text{for } x_i \in \{x, y, z\} \tag{7.126}$$

This leads to 9 derivatives:

$$\begin{array}{lll} \frac{\partial r}{\partial x} = \sin\vartheta\cos\varphi & \frac{\partial \vartheta}{\partial x} = \frac{1}{r}\cos\vartheta\cos\varphi & \frac{\partial \varphi}{\partial x} = -\frac{\sin\varphi}{r\sin\vartheta} \\ \frac{\partial r}{\partial y} = \sin\vartheta\sin\varphi & \frac{\partial \vartheta}{\partial y} = \frac{1}{r}\cos\vartheta\sin\varphi & \frac{\partial \varphi}{\partial y} = -\frac{\cos\varphi}{r\sin\vartheta} \\ \frac{\partial r}{\partial z} = \cos\vartheta & \frac{\partial \vartheta}{\partial z} = -\frac{\sin\vartheta}{r} & \frac{\partial \varphi}{\partial z} = 0 \end{array} \tag{7.127}$$

$$\Rightarrow \tag{7.128}$$

$$\frac{\partial}{\partial x} = \sin\vartheta\cos\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\vartheta\cos\varphi\frac{\partial}{\partial \vartheta} - \frac{\sin\varphi}{r\sin\vartheta}\frac{\partial}{\partial \varphi} \tag{7.129}$$

$$\frac{\partial}{\partial y} = \sin\vartheta\sin\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\vartheta\sin\varphi\frac{\partial}{\partial \vartheta} + \frac{\cos\varphi}{r\sin\vartheta}\frac{\partial}{\partial \varphi} \tag{7.130}$$

$$\frac{\partial}{\partial z} = \cos\vartheta\frac{\partial}{\partial r} - \frac{\sin\vartheta}{r}\frac{\partial}{\partial \vartheta} \tag{7.131}$$

If we insert (7.129, 7.130, 7.131) into the definition of L_i we get

$$L_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{7.132}$$

$$= \frac{\hbar}{i}\left\{ r\sin\vartheta\sin\varphi\left(\cos\vartheta\frac{\partial}{\partial r} - \frac{\sin\vartheta}{r}\frac{\partial}{\partial\vartheta}\right) - r\cos\vartheta\left(\sin\vartheta\sin\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\vartheta\sin\varphi\frac{\partial}{\partial\vartheta} + \frac{\cos\varphi}{r\sin\vartheta}\frac{\partial}{\partial\varphi}\right)\right\}$$

$$= \frac{\hbar}{i}\left((-\sin^2\vartheta\sin\varphi - \cos^2\vartheta\sin\varphi)\frac{\partial}{\partial\vartheta} - \frac{\cos\varphi\cos\vartheta}{\sin\vartheta}\frac{\partial}{\partial\varphi}\right)$$

$$L_x = \frac{\hbar}{i}\left(-\sin\varphi\frac{\partial}{\partial\vartheta} - \cos\varphi\cot\vartheta\frac{\partial}{\partial\varphi}\right)$$

In analogy to this transformation we get for the other operators

$$L_x = \frac{\hbar}{i}\left(-\sin\varphi\frac{\partial}{\partial\vartheta} - \cos\varphi\cot\vartheta\frac{\partial}{\partial\varphi}\right) \tag{7.133}$$

$$L_y = \frac{\hbar}{i}\left(\cos\varphi\frac{\partial}{\partial\vartheta} - \sin\varphi\cot\vartheta\frac{\partial}{\partial\varphi}\right) \tag{7.134}$$

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi} \tag{7.135}$$

$$L_+ = \hbar\, e^{i\varphi}\left(\frac{\partial}{\partial\vartheta} + i\cot\vartheta\frac{\partial}{\partial\varphi}\right) \tag{7.136}$$

$$L_- = \hbar\, e^{-i\varphi}\left(-\frac{\partial}{\partial\vartheta} + i\cot\vartheta\frac{\partial}{\partial\varphi}\right) \tag{7.137}$$

If we insert (7.136), (7.137) and (7.135) into (7.118) we get

$$\overrightarrow{L}^2 = L_+L_- + L_z^2 - \hbar L_z \tag{7.138}$$

$$\text{with } L_+L_- = \hbar^2 e^{i\varphi}\left(\frac{\partial}{\partial\vartheta} + i\cot\vartheta\frac{\partial}{\partial\varphi}\right)e^{-i\varphi}\left(-\frac{\partial}{\partial\vartheta} + i\cot\vartheta\frac{\partial}{\partial\varphi}\right)$$

$$= -\hbar^2\left(\frac{\partial^2}{\partial\vartheta^2} + \cot\vartheta\frac{\partial}{\partial\vartheta} + \cot^2\vartheta\frac{\partial^2}{\partial\varphi^2} + i\frac{\partial}{\partial\varphi}\right) \tag{7.139}$$

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi} \Rightarrow L_z^2 = -\hbar^2\frac{\partial^2}{\partial\varphi^2} \tag{7.140}$$

With the following

$$\cot^2\vartheta + 1 = \sin^{-2}\vartheta \tag{7.141}$$

$$\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta} = \frac{\partial^2}{\partial\vartheta^2} + \cot\vartheta\frac{\partial}{\partial\vartheta} \tag{7.142}$$

we get finally

$$\overrightarrow{L}^2 = -\hbar^2\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right). \tag{7.143}$$

The operators $\overrightarrow{L}^2$ and L_z do not depend on r or $\frac{\partial}{\partial r}$. Thus, they commute with $V(r)$. This is the result of $V(r)$ being invariant under rotations around the x-, y- or z-axis. Now, we have to transform H into spherical coordinates with $\triangle = \overrightarrow{\nabla} \bullet \overrightarrow{\nabla}$ and $\overrightarrow{\nabla}$ in spherical coordinates

$$\overrightarrow{\nabla} = \{\nabla_r,\, \nabla_\vartheta,\, \nabla_\varphi\} = \left\{ \frac{\partial}{\partial r},\, \frac{1}{r}\frac{\partial}{\partial \vartheta},\, \frac{1}{r\sin\vartheta}\frac{\partial}{\partial \varphi} \right\}. \tag{7.144}$$

For a vector $\overrightarrow{F}$ with the components $\overrightarrow{F} = \{F_r,\, F_\vartheta,\, F_\varphi\}$, $\overrightarrow{\nabla} \bullet \overrightarrow{F}$ is given by

$$\overrightarrow{\nabla} \bullet \overrightarrow{F} = \frac{1}{r^2 \sin\vartheta} \left\{ \frac{\partial}{\partial r}(r^2(\sin\vartheta)F_r) + \frac{\partial}{\partial \vartheta}(r(\sin\vartheta)F_\vartheta) + \frac{\partial}{\partial \varphi}(rF_\varphi) \right\}. \tag{7.145}$$

Using $\overrightarrow{F} = \overrightarrow{\nabla}$ we have

$$\begin{aligned} \triangle &= \overrightarrow{\nabla} \bullet \overrightarrow{\nabla} \\ &= \frac{1}{r^2 \sin\vartheta} \left\{ \frac{\partial}{\partial r}(r^2 \sin\vartheta \frac{\partial}{\partial r}) + \frac{\partial}{\partial \vartheta} \sin\vartheta \frac{\partial}{\partial \vartheta} + \frac{\partial}{\partial \varphi} \frac{1}{\sin\vartheta} \frac{\partial}{\partial \varphi} \right\} \qquad (7.146) \\ \triangle &= \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial \vartheta} \sin\vartheta \frac{\partial}{\partial \vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial \varphi^2} \right). \qquad (7.147) \end{aligned}$$

The Hamilton operator is

$$\begin{aligned} H &= -\frac{\hbar^2}{2m}\triangle + V(r) \qquad (7.148) \\ &= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\hbar^2}{2mr^2}\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial \vartheta}\sin\vartheta\frac{\partial}{\partial \vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial \varphi^2} \right) + V(r) \\ H &= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\overrightarrow{L}^2}{2mr^2} + V(r). \qquad (7.149) \end{aligned}$$

Since $\overrightarrow{L}^2$ and L_z depend on $(\vartheta,\, \varphi,\, \frac{\partial}{\partial \vartheta},\, \frac{\partial}{\partial \varphi},\, \frac{\partial^2}{\partial \vartheta^2},\, \frac{\partial^2}{\partial \varphi^2})$ and $V(r)$ and the other terms depend on $(r,\, \frac{\partial}{\partial r},\, \frac{\partial^2}{\partial r^2})$ it is

$$[H, \overrightarrow{L}^2] = 0 \quad [H, L_z] = 0 \quad \text{if} \quad V(\overrightarrow{r}) = V(r). \tag{7.150}$$

The eigenfunctions $\Phi(\varphi)$ of L_z satisfy the eigenfunction equation

$$L_z \Phi(\varphi) = m\hbar\Phi(\varphi) \tag{7.151}$$

where the eigenvalues have been written as $m\hbar$ for convenience. The normalized solutions of (7.151) are

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}. \tag{7.152}$$

Since the functions $\Phi_m(\varphi)$ must be single-valued, we have $\Phi_m(2\pi) = \Phi_m(0)$, and m is restricted to positive or negative integers or zero $m = \{0, \pm 1, \pm 2, \ldots\}$. The integer m is called the *magnetic quantum number* with orthonormal eigenfunctions

$$\int_0^{2\pi} \Phi^*_{m'}(\varphi)\Phi_m(\varphi)d\varphi = \delta_{m,m'}. \tag{7.153}$$

The simultaneous eigenfunctions of $\overrightarrow{L}^2$ and L_z (remember $[\overrightarrow{L}^2, L_z] = 0$) are called *spherical harmonics* and are denoted by $Y_{\ell m}(\vartheta, \varphi)$. They satisfy the eigenvalue equations

$$\begin{aligned} \overrightarrow{L}^2 Y_{\ell m}(\vartheta,\varphi) &= \ell(\ell+1)\hbar^2 Y_{\ell m}(\vartheta,\varphi) && (7.154)\\ L_z Y_{\ell m}(\vartheta,\varphi) &= m\hbar Y_{\ell m}(\vartheta,\varphi) && (7.155) \end{aligned}$$

where the eigenvalues of $\overrightarrow{L}^2$ have been written as $\ell(\ell+1)\hbar^2$. The quantum number ℓ is known as the *orbital angular momentum quantum number*. The number $\ell(\ell+1)$ is dimensionless and has to be positive or zero, because it is the eigenvalue of the squared hermitian operator. Possible values for ℓ are given by

$$\begin{aligned} L_z^2 Y_{\ell m}(\vartheta,\varphi) &= m^2\hbar^2 Y_{\ell m}(\vartheta,\varphi) \\ (L_x^2 + L_y^2) Y_{\ell m}(\vartheta,\varphi) &= (\overrightarrow{L}^2 - L_z^2) Y_{\ell m}(\vartheta,\varphi) \\ &= [\ell(\ell+1) - m^2]\hbar^2 Y_{\ell m}(\vartheta,\varphi) \\ \int Y^*_{\ell m}(\vartheta,\varphi)(L_x^2+L_y^2)Y_{\ell m}(\vartheta,\varphi)d\overrightarrow{r} &= \hbar^2[\ell(\ell+1)-m^2]\int Y^*_{\ell m}(\vartheta,\varphi)Y_{\ell m}(\vartheta,\varphi)d\overrightarrow{r} \\ &= \langle L_x^2 + L_z^2\rangle \geq 0 && (7.156)\\ \Rightarrow m^2 &\leq \ell(\ell+1) = \ell^2 + \ell && (7.157) \end{aligned}$$

In equation (7.156) we used that the expectation value of a squared hermitian operator is positive or zero. In equation (7.138) we expressed $\overrightarrow{L}^2$ with the lowering and rising operators L_+ and L_-. Since $L_\pm$ commute with $\overrightarrow{L}^2$ ($L_\pm$ commute with L_z see exercise) it satisfy the equation

$$\begin{aligned} \overrightarrow{L}^2 L_\pm Y_{\ell m}(\vartheta,\varphi) &= L_\pm \overrightarrow{L}^2 Y_{\ell m}(\vartheta,\varphi) = L_\pm \ell(\ell+1)\hbar^2 Y_{\ell m}(\vartheta,\varphi) \\ &= \ell(\ell+1)\hbar^2 L_\pm Y_{\ell m}(\vartheta,\varphi) && (7.158) \end{aligned}$$

$L_\pm$ and $\overrightarrow{L}^2$ have the same eigenfunctions and if the lowering or rising operator acts on $Y_{\ell lm}(\vartheta,\varphi)$ it does not change the eigenvalues $\ell(\ell+1)\hbar^2$ of $\overrightarrow{L}^2$. But the operator $L_\pm$ changes the eigenvalues of L_z, because with $[L_\pm, L_z] = \mp\hbar L_\pm$ it is

$$\begin{aligned} L_z(L_\pm Y_{\ell m}(\vartheta,\varphi)) &= L_\pm L_z Y_{\ell m}(\vartheta,\varphi) \pm \hbar L_\pm Y_{\ell m}(\vartheta,\varphi) \\ &= (m \pm 1)\hbar(L_\pm Y_{\ell m}(\vartheta,\varphi)). && (7.159) \end{aligned}$$

That means $L_{\pm}Y_{\ell m}(\vartheta,\varphi)$ are eigenfunctions of L_z to the eigenvalue $(m+1)\hbar$. The operator $L_{\pm}$ increases (+) or decreases (-) the value of the magnetic quantum number by one:

$$L_{\pm}Y_{\ell m}(\vartheta,\varphi) \propto Y_{\ell\,(m\pm1)}(\vartheta,\varphi) \tag{7.160}$$

The rising and lowering of m is limited by $\ell\,(\ell+1)$, so that there is a maximum value of m called m_{max} and a minimum value of m called m_{min} which satisfy the equations

$$L_{+}Y_{\ell\,m_{max}}(\vartheta,\varphi) = 0 \tag{7.161}$$
$$L_{-}Y_{\ell\,m_{min}}(\vartheta,\varphi) = 0. \tag{7.162}$$

Using the operator L_{-}, L_{+} and equations (7.161, 7.162) we find that

$$\begin{aligned}
L_{-}L_{+}Y_{\ell\,m_{max}}(\vartheta,\varphi) &= (\overrightarrow{L}^2 - L_z^2 - \hbar L_z)Y_{\ell\,m_{max}}(\vartheta,\varphi) && (7.163)\\
&= \hbar^2[\ell\,(\ell+1) - m_{max}^2 - m_{max}]Y_{\ell\,m_{max}}(\vartheta,\varphi) && (7.164)\\
L_{-}L_{+}Y_{\ell\,m_{max}}(\vartheta,\varphi) &= 0 && (7.165)\\
L_{+}L_{-}Y_{\ell\,m_{min}}(\vartheta,\varphi) &= (\overrightarrow{L}^2 - L_z^2 + \hbar L_z)Y_{\ell\,m_{min}}(\vartheta,\varphi) && (7.166)\\
&= \hbar^2[\ell\,(\ell+1) - m_{min}^2 + m_{min}]Y_{\ell\,m_{min}}(\vartheta,\varphi) && (7.167)\\
L_{+}L_{-}Y_{\ell\,m_{min}}(\vartheta,\varphi) &= 0 && (7.168)
\end{aligned}$$

Since the eigenfunctions $Y_{\ell m}(\vartheta,\varphi)$ are not identical zero it is

$$\begin{aligned}
m_{max}(m_{max}+1) &= \ell\,(\ell+1) \geq 0 && (7.169)\\
m_{min}(m_{min}-1) &= \ell\,(\ell+1) \geq 0 && (7.170)\\
\Rightarrow m_{min}(m_{min}-1) &\overset{m_{min}=-\ell}{=} -\ell\,(-\ell-1) = \ell\,(\ell+1) && (7.171)
\end{aligned}$$

We showed already that the magnetic quantum numbers m are integers and from equations (7.169, 7.170) we can conclude that the orbital angular momentum quantum numbers ℓ are also integers. Since the rising and lowering operators L_{+} and L_{-} increases and decreases m by one, the values of the magnetic quantum number are

$$-\ell \leq m \leq \ell\,. \tag{7.172}$$

Thus, for a given orbital angular momentum quantum number ℓ the magnetic quantum number m can take $(2\ell+1)$ values

$$m = \{0,\,\pm1,\,\pm2,\,\ldots,\,\pm\ell\,\}. \tag{7.173}$$

The eigenvalue equations are

$$\begin{aligned}
\overrightarrow{L}^2 Y_{\ell m}(\vartheta,\varphi) &= \hbar^2\ell\,(\ell+1)\,Y_{\ell m}(\vartheta,\varphi) && (7.174)\\
L_z Y_{\ell m}(\vartheta,\varphi) &= \hbar\,m\,Y_{\ell m}(\vartheta,\varphi), \quad -\ell \leq \mathrm{m} \leq +\ell && (7.175)
\end{aligned}$$

If $Y_{\ell,-\ell}(\vartheta,\varphi)$ or $Y_{\ell\ell}(\vartheta,\varphi)$ are known, we can use the operators L_+ and L_- to generate all other eigenfunctions $Y_{\ell m}(\vartheta,\varphi)$, in analogy to the harmonic oscillator eigenfunctions. For the maximum value of $m=\ell$ one has

$$\begin{aligned} L_+ Y_{\ell\ell}(\vartheta,\varphi) &= 0 \\ \Rightarrow \hbar e^{i\varphi}\left[\frac{\partial}{\partial\vartheta}+i\cot\vartheta\frac{\partial}{\partial\varphi}\right]Y_{\ell\ell}(\vartheta,\varphi) &= 0 \qquad (7.176) \\ L_z Y_{\ell\ell}(\vartheta,\varphi)=\frac{\hbar}{i}\frac{\partial}{\partial\varphi}Y_{\ell\ell}(\vartheta,\varphi) &= \hbar\,\ell\; Y_{\ell\ell}(\vartheta,\varphi) \qquad (7.177) \end{aligned}$$

We know from equation (7.177) that $\frac{\partial}{\partial\varphi}Y_{\ell m}(\vartheta,\varphi)$ does not depend on ϑ, and we solve the (7.176) by using the product solution method. Setting

$$\begin{aligned} Y_{\ell m}(\vartheta,\varphi) &= P_\ell^m(\vartheta)\Phi_m(\varphi) \qquad (7.178) \\ \overset{m=\ell}{\Rightarrow} Y_{\ell\ell}(\vartheta,\varphi) &= P_\ell^\ell(\vartheta)\Phi_\ell(\varphi) \qquad (7.179) \\ \hbar e^{i\varphi}\left[\frac{\partial}{\partial\vartheta}+i\cot\vartheta\frac{\partial}{\partial\varphi}\right]P_\ell^\ell(\vartheta)\Phi_\ell(\varphi) &= 0 \qquad (7.180) \\ \Phi_\ell(\varphi)\frac{\partial}{\partial\vartheta}P_\ell^\ell(\vartheta)+i\cot\vartheta P_\ell^\ell(\vartheta)\frac{\partial}{\partial\varphi}\Phi_\ell(\varphi) &= 0 \qquad (7.181) \\ \Phi_\ell(\varphi)\tan\vartheta\frac{\partial}{\partial\vartheta}P_\ell^\ell(\vartheta) &= -iP_\ell^\ell(\vartheta)\frac{\partial}{\partial\varphi}\Phi_\ell(\varphi) \qquad (7.182) \\ \frac{\tan\vartheta}{P_\ell^\ell(\vartheta)}\frac{\partial}{\partial\vartheta}P_\ell^\ell(\vartheta) &= \frac{-i}{\Phi_\ell(\varphi)}\frac{\partial}{\partial\varphi}\Phi_\ell(\varphi)=c \qquad (7.183) \\ \Rightarrow \frac{\partial}{\partial\vartheta}P_\ell^\ell(\vartheta) &= c\,\frac{\cos\vartheta}{\sin\vartheta}\,P_\ell^\ell(\vartheta) \qquad (7.184) \\ \Rightarrow \frac{\partial}{\partial\varphi}\Phi_\ell(\varphi) &= ic\,\Phi_\ell(\varphi) \qquad (7.185) \end{aligned}$$

With equation (7.177) the constant c has to be $c=\ell$.

$$\begin{aligned} \Phi_\ell(\varphi) &\propto e^{i\ell\varphi} \\ P_\ell^\ell(\vartheta) &\propto \sin^\ell\vartheta \\ \Rightarrow Y_{\ell\ell}(\vartheta,\varphi) &\propto \sin^\ell\vartheta e^{i\ell\varphi} \qquad (7.186) \\ \Rightarrow Y_{\ell m}(\vartheta,\varphi) &\propto P_\ell^m(\vartheta)e^{im\varphi} \qquad (7.187) \end{aligned}$$

Using L_- iteratively we get the complete set of $2\ell+1$ eigenfunctions $\{Y_{\ell m}(\vartheta,\varphi)\}$. The functions $P_\ell^0(\cos\vartheta)$ are called the Legendre polynomials of degree ℓ. They are defined by the relation

$$P_\ell(\cos\vartheta)=\frac{1}{2^\ell\,\ell!}\frac{d^\ell}{d(\cos\vartheta)^\ell}((\cos\vartheta)^2-1)^\ell. \qquad (7.188)$$

The Legendre polynomials ($m = 0$) satisfy the differential equation

$$\left[(1-\cos^2\vartheta)\frac{d^2}{d(\cos\vartheta)^2} - 2\cos\vartheta\frac{d}{d\cos\vartheta} + \ell(\ell+1)\right] P_\ell(\cos\vartheta) = 0 \tag{7.189}$$

with the recurrence relation

$$(2\ell+1)\cos\vartheta P_\ell - (\ell+1)P_{\ell+1} - \ell P_{\ell-1} = 0 \tag{7.190}$$

which is also valid for $\ell = 0$ if one defines $P_{-\ell} = 0$. The orthogonality relations read

$$\int_{-1}^{+1} P_\ell(\cos\vartheta)P_{\ell'}(\cos\vartheta)d\cos\vartheta = \frac{2}{2\ell+1}\delta_{\ell\ell'}. \tag{7.191}$$

One has the closure relation

$$\frac{1}{2}\sum_{\ell=0}^{\infty}(2\ell+1)P_\ell(\cos\vartheta)P_\ell(\cos\vartheta') = \delta(\cos\vartheta - \cos\vartheta') \tag{7.192}$$

Important particular values of the Legendre polynomials are

$$\cos\vartheta = 1 \;:\quad P_\ell(1) = 1, \quad \cos\vartheta = -1 \;:\quad P_\ell(-1) = (-1)^\ell \tag{7.193}$$

For the lowest values of ℓ one has explicitly

$$P_0(\cos\vartheta) = 1 \tag{7.194}$$
$$P_1(\cos\vartheta) = \cos\vartheta \tag{7.195}$$
$$P_2(\cos\vartheta) = \frac{1}{2}\left(3\cos^2\vartheta - 1\right) \tag{7.196}$$
$$P_3(\cos\vartheta) = \frac{1}{2}\left(5\cos^3\vartheta - 3\cos\vartheta\right) \tag{7.197}$$
$$P_4(\cos\vartheta) = \frac{1}{8}\left(35\cos^4\vartheta - 30\cos^2\vartheta + 3\right) \tag{7.198}$$
$$P_5(\cos\vartheta) = \frac{1}{8}\left(63\cos^5\vartheta - 70\cos^3\vartheta + 15\cos\vartheta\right) \tag{7.199}$$

The associated Legendre functions $P_\ell^m(\cos\vartheta)$ are now defined by the relations

$$P_\ell^m(\cos\vartheta) = (1-\cos^2\vartheta)^{m/2}\frac{d^m}{d(\cos\vartheta)^m}P_\ell(\cos\vartheta), \quad \mathrm{m} = 0,\ 1,\ 2,\ \ldots,\ \ell. \tag{7.200}$$

They satisfy the recurrence relations

$$(2\ell+1)\cos\vartheta\, P_\ell^m = (\ell+1-m)P_{\ell+1}^m + (\ell+m)P_{\ell-1}^m \tag{7.201}$$
$$(2\ell+1)\sqrt{(1-\cos^2\vartheta)}P_\ell^{m-1} = P_{\ell+1}^m - P_{\ell-1}^m \tag{7.202}$$

and the orthogonality relations

$$\int_{-1}^{1} P_\ell^m(\cos\vartheta) P_{\ell'}^m(\cos\vartheta) d\cos\vartheta = \frac{2}{2\ell+1}\frac{(l+m)!}{(l-m)!}\,\delta_{\ell\,\ell'} \tag{7.203}$$

The first few associated Legendre functions are given explicitly by

$$\begin{aligned}
P_1^1(\cos\vartheta) &= \sqrt{(1-\cos^2\vartheta)} && (7.204)\\
P_2^1(\cos\vartheta) &= 3\sqrt{(1-\cos^2\vartheta)}\cos\vartheta && (7.205)\\
P_2^2(\cos\vartheta) &= 3(1-\cos^2\vartheta) && (7.206)\\
P_3^1(\cos\vartheta) &= \frac{3}{2}\sqrt{(1-\cos^2\vartheta)}(5\cos^2\vartheta-1) && (7.207)\\
P_3^2(\cos\vartheta) &= 15\cos\vartheta(1-\cos^2\vartheta) && (7.208)\\
P_3^3(\cos\vartheta) &= 15\sqrt{1-\cos^2\vartheta}(1-\cos^2\vartheta) && (7.209)
\end{aligned}$$

Thus, the spherical harmonics $Y_{\ell m}(\vartheta,\varphi)$ with $m \geq 0$ are given by

$$\begin{aligned}
Y_{\ell m}(\vartheta,\varphi) &= (-1)^m\sqrt{\left[\frac{(2\ell+1)(l-m)!}{4\pi(l+m)!}\right]}P_\ell^m(\cos\vartheta)e^{im\varphi} && (7.210)\\
Y_{\ell -m}(\vartheta,\varphi) &= (-1)^m Y_{\ell m}^*(\vartheta,\varphi) && (7.211)
\end{aligned}$$

The first few spherical harmonics are given explicitly by

$$\begin{aligned}
(2\ell+1)\quad & Y_{\ell m}(\vartheta,\varphi)\\
1\quad & Y_{0\,0}(\vartheta,\varphi) = \frac{1}{\sqrt{4\pi}}\\
3\quad & Y_{1\,0}(\vartheta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\vartheta = \sqrt{\frac{3}{4\pi}}\,\frac{z}{r}\\
3\quad & Y_{1\,\pm1}(\vartheta,\varphi) = \mp\sqrt{\frac{3}{8\pi}}\sin\vartheta\, e^{\pm i\varphi} = \mp\sqrt{\frac{3}{8\pi}}\frac{x\pm iy}{r}\\
5\quad & Y_{2\,0}(\vartheta,\varphi) = \sqrt{\frac{5}{4\pi}}\left(\frac{3}{2}\cos^2\vartheta-\frac{1}{2}\right) = \frac{1}{2}\sqrt{\frac{5}{4\pi}}\frac{2z^2-x^2-y^2}{r^2}\\
5\quad & Y_{2\,\pm1}(\vartheta,\varphi) = \mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\vartheta\cos\vartheta\, e^{\pm i\varphi} = \mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\frac{(x\pm iy)z}{r^2}\\
5\quad & Y_{2\,\pm2}(\vartheta,\varphi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\vartheta\, e^{\pm 2i\varphi} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\left(\frac{x\pm iy}{r}\right)^2
\end{aligned}$$

The rising and lowering operators are

$$L_- Y_{\ell m}(\vartheta,\varphi) = -\hbar e^{-i\varphi}\left[-\frac{\partial}{\partial\vartheta} + m\,\cot\vartheta\right] Y_{\ell m}(\vartheta,\varphi) \tag{7.212}$$

$$L_+ Y_{\ell m}(\vartheta,\varphi) = -\hbar e^{i\varphi}\left[\frac{\partial}{\partial\vartheta} + m\,\cot\vartheta\right] Y_{\ell m}(\vartheta,\varphi) \tag{7.213}$$

$$L_\pm Y_{\ell m}(\vartheta,\varphi) = \hbar\sqrt{\ell(\ell+1) - m(m\pm 1)}\; Y_{\ell m\pm 1}(\vartheta,\varphi) \tag{7.214}$$

$$L_\pm |\ell m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m\pm 1)}\; |\ell m\pm 1\rangle \tag{7.215}$$

and they change the magnetic quantum number (Fig. 7.3)

$$L_- Y_{11}(\vartheta,\varphi) \propto \hbar e^{-i\varphi}\left[-\frac{\partial}{\partial\vartheta} + m\,\cot\vartheta\right] \sin\vartheta e^{i\varphi} \tag{7.216}$$

$$\propto Y_{10} \tag{7.217}$$

$$L_- Y_{10} \propto Y_{1-1} \tag{7.218}$$

The absolute values of the spherical harmonics are given by the associated Le-

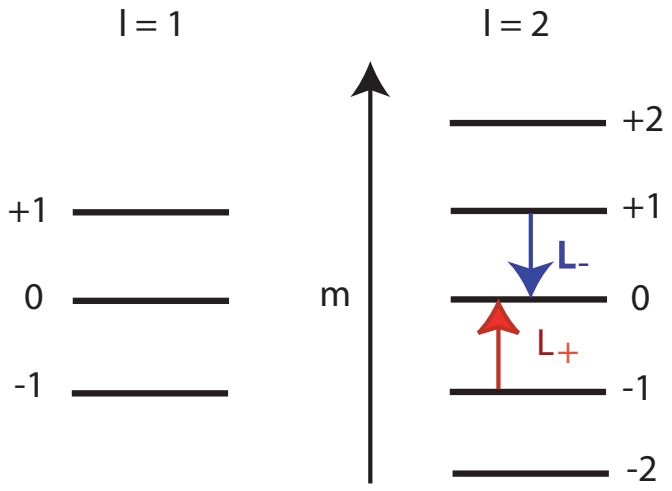


Abbildung 7.4. Operations of the rising and lowering operator on the magnetic quantum number m.

gendre functions $|P_l^m(\vartheta)|$ which are presented in Fig. 7.3. The polar plots give the length of $|P_l^m(\vartheta)|$ for every angle ϑ. Since ϑ varies from 0 to π the polar plots have axial symmetry with respect to the z-axis. The set of eigenfunctions $\{Y_{\ell m}(\vartheta,\varphi)\}$ are eigenfunctions of the hermitian operator $\overrightarrow{L}^2$. They form a orthonormal complete set of functions with

$$\int\int Y^*_{\ell m}(\vartheta,\varphi) Y_{\ell' m'}(\vartheta,\varphi)\sin\vartheta d\vartheta d\varphi = \delta_{\ell\ell'}\delta_{mm'}. \tag{7.219}$$

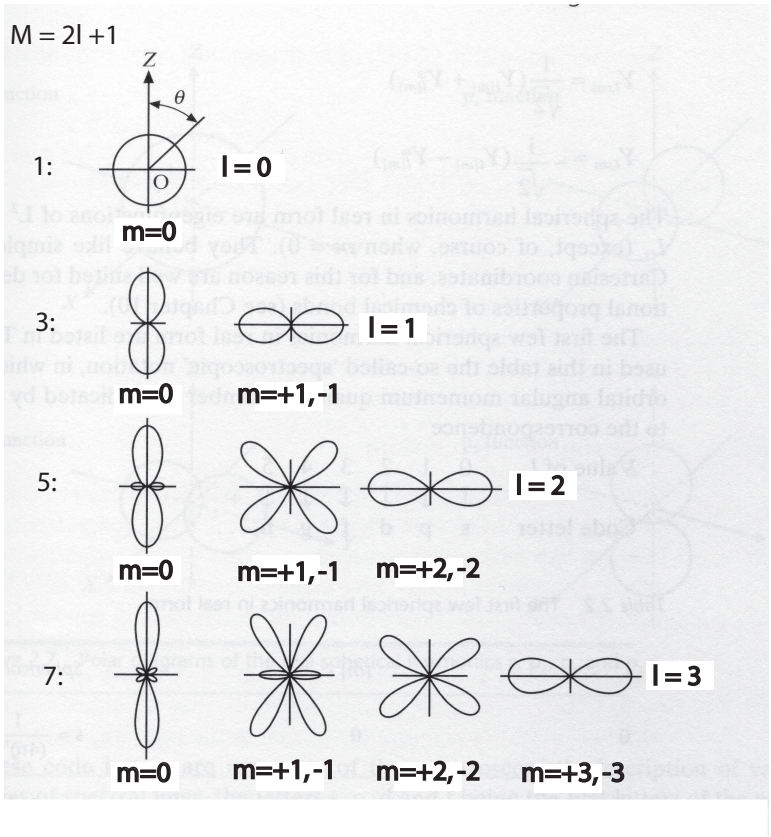


Abbildung 7.5. Polar plots of the Legendre polynomials $|Y_{\ell m}(\vartheta,\varphi)| = \frac{1}{2\pi}|P_\ell^m|^2$. For every orbital momentum quantum number ℓ there are $2\ell+1$ eigenfunctions.

Every square integrable function $\psi(\vartheta,\varphi)$ can be developed by $\{Y_{\ell m}(\vartheta,\varphi)\}$

$$\psi(\vartheta,\varphi) = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{+\ell} c_{\ell m} Y_{\ell m}(\vartheta,\varphi) \tag{7.220}$$

Some properties of the eigenfunctions are

$$\begin{aligned}
Y^*_{\ell m}(\vartheta,\varphi) &= (-1)^m Y_{\ell -m}(\vartheta,\varphi) && (7.221)\\
P_\ell^{-m} &= P_\ell^m \quad \text{by definition m} \geq 0 && (7.222)\\
\overrightarrow{r} \to -\overrightarrow{r} \quad Y_{\ell m}(\pi-\vartheta,\varphi+\pi) &= (-1)^\ell Y_{\ell m}(\vartheta,\varphi) && (7.223)\\
P^0_\ell(\cos(\pi-\vartheta)) &= (-1)^\ell P^0_\ell(\cos\vartheta) && (7.224)\\
Y_{\ell m}(\vartheta,\varphi+2\pi) &= Y_{\ell m}(\vartheta,\varphi)e^{im\varphi} = Y_{\ell m}(\vartheta,\varphi) && (7.225)
\end{aligned}$$

The $Y_{\ell m}(\vartheta,\varphi)$ are complex functions for $m \neq 0$. It is useful for chemical bond orbitals to create a linear combination of $Y_{\ell m}(\vartheta,\varphi)$ and $Y_{\ell -m}(\vartheta,\varphi)$ which are real

functions. Note, they are no longer eigenfunctions of L_z. Examples are

$$\frac{1}{\sqrt{2}}(Y_{1-1}(\vartheta,\varphi) - Y_{11}(\vartheta,\varphi)) = \sqrt{\frac{3}{4\pi}}\frac{1}{2}\sin\vartheta\left(e^{-i\varphi} + e^{i\varphi}\right) \quad (7.226)$$

$$= \sqrt{\frac{3}{4\pi}}\sin\vartheta\cos\varphi = \sqrt{\frac{3}{4\pi}}\frac{x}{r} \quad (7.227)$$

$$\frac{1}{\sqrt{2}}i(Y_{1-1}(\vartheta,\varphi) + Y_{11}(\vartheta,\varphi)) = \sqrt{\frac{3}{4\pi}}\frac{1}{2}i\sin\vartheta\left(e^{-i\varphi} - e^{i\varphi}\right) \quad (7.228)$$

$$= \sqrt{\frac{3}{4\pi}}\sin\vartheta\sin\varphi = \sqrt{\frac{3}{4\pi}}\frac{y}{r} \quad (7.229)$$

$$Y_{10}(\vartheta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\vartheta = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \quad (7.230)$$

These three linear combinations form the three orbitals in the directions of the x-axis (p_x), the y-axis (p_y) and the z-axis (p_z) as shown in Fig. (7.3). The few

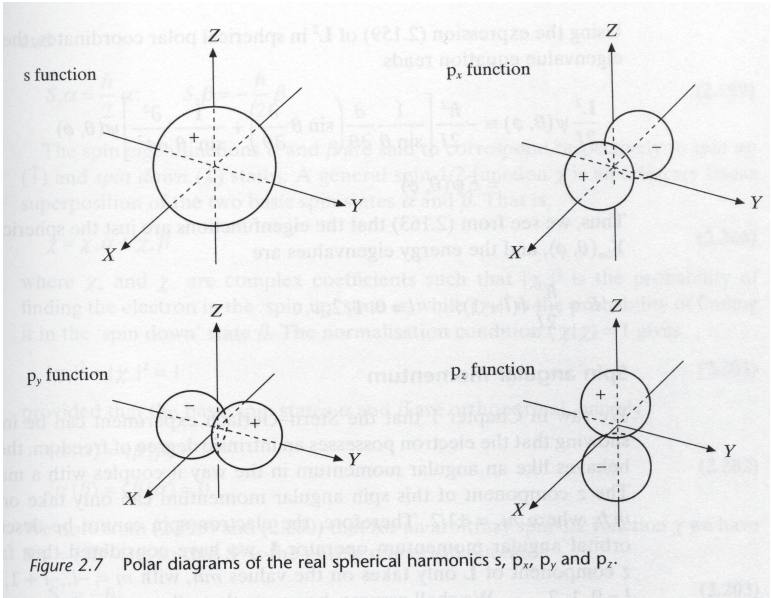


Figure 2.7 Polar diagrams of the real spherical harmonics s, p$_x$, p$_y$ and p$_z$.

Abbildung 7.6. Polar plots of the real spherical harmonics s, p_x, p_y, p_z.

first spherical harmonics in real form ${}_rY_{\ell m}(\vartheta,\varphi)$ are

$$\begin{array}{cccc} \ell & |m| & & {}_rY_{\ell m}(\vartheta,\varphi) \end{array} \tag{7.231}$$

$$0 \quad 0 \qquad s: \qquad \frac{1}{\sqrt{4\pi}} \tag{7.232}$$

$$1 \quad 0 \qquad p_z: \qquad \sqrt{\frac{3}{4\pi}}\cos\vartheta \tag{7.233}$$

$$1 \quad 1 \qquad p_x: \qquad \sqrt{\frac{3}{4\pi}}\sin\vartheta\cos\varphi \tag{7.234}$$

$$1 \quad 1 \qquad p_y: \qquad \sqrt{\frac{3}{4\pi}}\sin\vartheta\sin\varphi \tag{7.235}$$

$$2 \quad 0 \qquad d_{3z^2-r^2}: \qquad \sqrt{\frac{5}{16\pi}}(3\cos^2\varphi - 1) \tag{7.236}$$

$$2 \quad 1 \qquad d_{xz}: \qquad \sqrt{\frac{15}{4\pi}}\sin\vartheta\cos\vartheta\cos\varphi \tag{7.237}$$

$$2 \quad 1 \qquad d_{yz}: \qquad \sqrt{\frac{15}{4\pi}}\sin\vartheta\cos\vartheta\sin\varphi \tag{7.238}$$

$$2 \quad 2 \qquad d_{x^2-y^2}: \qquad \sqrt{\frac{15}{4\pi}}\sin^2\vartheta\cos 2\varphi \tag{7.239}$$

$$2 \quad 2 \qquad d_{xy}: \qquad \sqrt{\frac{15}{4\pi}}\sin^2\vartheta\sin 2\varphi \tag{7.240}$$

Here, we have used the so-called 'spectroscopic' notation, in which the value of the orbital angular momentum quantum number ℓ is indicated by a letter, according to the correspondence

$$\text{Value of } \ell \qquad 0 \;\; 1 \;\; 2 \;\; 3 \;\; 4 \;\; 5 \;\; \ldots \tag{7.241}$$

$$\updownarrow \;\; \updownarrow \;\; \updownarrow \;\; \updownarrow \;\; \updownarrow \;\; \updownarrow \;\; \ldots \tag{7.242}$$

$$\text{Code letter} \qquad s \;\; p \;\; d \;\; f \;\; g \;\; h, \ldots \tag{7.243}$$

These code letters are remnants of the spectroscopist's description of various series of spectral lines. The letters s, p, d and f being the first letters of the adjectives 'sharp', 'principal', 'diffuse' and 'fundamental', respectively. For values of ℓ greater than three the letters follow in alphabetical order.

8 Hydrogen atom and central forces

8.1 Central forces

For central forces the potential $V(\overrightarrow{r}) = V(r)$ depends only on $|\overrightarrow{r}|$ and the eigenfunctions are simultaneous eigenfunctions of H, $\overrightarrow{L}^2$ and L_z. We can solve

the SE with the product solution method. Setting

$$\psi_{n\ell m}(r,\vartheta,\varphi) = R_{n\ell}(r)Y_{\ell m}(\vartheta,\varphi) \tag{8.1}$$

and substituting into (7.149) gives

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\overrightarrow{L}^2}{2mr^2} + V(r)\right] R_{n\ell}(r)Y_{\ell m}(\vartheta,\varphi) \quad = \quad E_{n\ell m}R_{n\ell}(r)Y_{\ell m}(\vartheta,\varphi) \tag{8.2}$$

From $\overrightarrow{L}^2 Y_{\ell m} = \ell(\ell+1)\hbar^2 Y_{\ell m}$ we deduce

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r)\right] R_{n\ell}(r) = E_{n\ell m}R_{n\ell}(r) \tag{8.3}$$

Equation (8.3) does not depend on the magnetic quantum number m. Setting

$$u_{n\ell}(r) = rR_{n\ell}(r) \tag{8.4}$$

we find

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r)\right] u_{n\ell}(r) = E_{n\ell}u_{n\ell}(r) \tag{8.5}$$

The radial SE is a one dimensional differential equation in r, $r \in (0,\infty)$. We define the effective potential V_{eff}

$$V_{eff}(r) = V(r) + \frac{\ell(\ell+1)}{2mr^2} \tag{8.6}$$

The second term is known as the 'centrifugal barrier' potential (with $2mr^2$ as the moment of inertia), from the classical mechanics. With $V(r) = -\frac{Ze}{4\pi\varepsilon_0 r}$ the attractive potential of the Coulomb interaction is stronger than the 'centrifugal barrier' potential for large $r \to \infty$. For small r the 'centrifugal barrier' potential dominates resulting in a minimum shifting to larger r upon increasing the orbital angular momentum quantum number ℓ (see Fig. 8.1). The probability of finding an electron in the vicinity of the nucleus decreases with increasing ℓ.

8.2 Radial functions

The asymptotic properties of the radial functions $R_{n\ell}$ are

- for $r \to \infty$ it is $V_{eff} \to 0$ and

$$u_{n\ell}(r) \quad \propto \quad e^{-r\sqrt{\frac{2|E_{n\ell}|m}{\hbar^2}}} \tag{8.7}$$

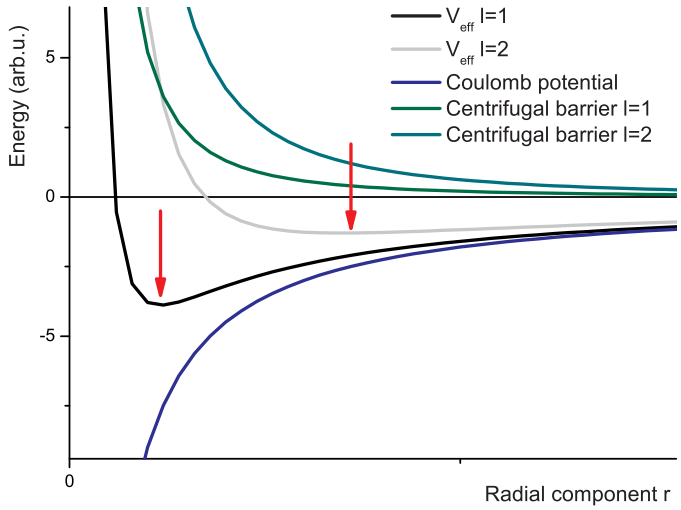


Abbildung 8.1. Potential components contributing to the Hamilton operator.

- for $r \to 0$ it is $V_{eff} \to \frac{\ell(\ell+1)\hbar^2}{2mr^2}$ and with $E_{n\ell} \approx 0$

$$u_{n\ell}(r) \propto r^{\ell+1} \tag{8.8}$$

Thus, we find the asymptotic correct solution

$$R_{n\ell} = \frac{u_{n\ell}}{r} \propto r^{\ell} e^{-r\sqrt{\frac{2|E_{n\ell m}|}{\hbar^2}}} \tag{8.9}$$

For a hydrogen atom ($Z = 1$) and similar atom ions the Coulomb potential is given by

$$V(r) = -\frac{Ze}{4\pi\varepsilon_0 r} \tag{8.10}$$

There are two ways of solving the partial differential equation

1) describing H as a product of a and a^+

2) using $u_{n\ell}$ and its power series one finds the differential equation

$$z\frac{d^2w}{dz^2} + (c - z)\frac{dw}{dz} - aw = 0 \tag{8.11}$$

which is called the *Kummer-Laplace differential equation* and can be solved for $c = 1$ and $a = 0$. The functions which satisfy the differential equation are called the *associated Laguerre polynomials* $L^{2\ell+1}_{n+\ell}(\alpha_{n\ell}\, r)$ given explicitly by

$$L^{2\ell+1}_{n+\ell}(r) = \sum_{k=0}^{n-\ell-1} (-1)^{k+1} \frac{[(n+\ell)!]^2\, r^k}{(n-\ell-1-k)!(2\ell+1+k)!k!}. \tag{8.12}$$

The *Laguerre polynomials* are special solutions only for hydrogen atoms and similar atomic ions and the radial functions are given explicitly by

$$R_{n\ell}(\rho) = \widehat{N}_{n\ell} \cdot (\rho)^{\ell}\, L_{n+\ell}^{2\ell+1}(\rho)\, e^{-\rho/2} \tag{8.13}$$

$$\text{with } \mu = \frac{mM}{m+M}, \quad a_\mu = \frac{a_0 m}{\mu} \quad \rho = \frac{2Zr}{na_\mu} \quad \text{and} \quad \alpha_n = \frac{Z}{na_0} \tag{8.14}$$

$$R_{n\ell}(r) = N_{n\ell} \cdot (\alpha_n r)^{\ell}\, L_{n+\ell}^{2\ell+1}(2\alpha_n r)\, e^{-\alpha_n r} \tag{8.15}$$

$$\text{with } E_n = -\sqrt{\frac{mZ^2e^4}{2\hbar^2(4\pi\varepsilon_0)^2 n^2}} = -\frac{\hbar^2\alpha_n^2}{2m} \tag{8.16}$$

$$\frac{1}{\alpha_n} = \frac{na_0}{Z}, \quad \text{characteristic length} \quad \mathrm{a_0} = 0.529\ \mathring{\mathrm{A}} \tag{8.17}$$

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}} \tag{8.18}$$

$$R_{20}(r) = 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \left(1 - \frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}} \tag{8.19}$$

$$R_{21}(r) = \frac{2}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}} \tag{8.20}$$

$$R_{30}(r) = 2\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}} \left(1 - \frac{2Zr}{3a_0} + \frac{2Z^2r^2}{27a_0^2}\right) e^{-\frac{Zr}{3a_0}} \tag{8.21}$$

$$R_{31}(r) = \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{3a_0}\left(1 - \frac{Zr}{6a_0}\right)\right) e^{-\frac{Zr}{3a_0}} \tag{8.22}$$

$$R_{32}(r) = \frac{2\sqrt{2}}{3\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}} \left(\frac{Zr}{3a_0}\right)^2 e^{-\frac{Zr}{3a_0}} \tag{8.23}$$

Because the spherical harmonics are normalized on the unit sphere the normalization condition implies that

$$\int_0^\infty R_{n\ell}(r)\, r^2\, dr = 1 \tag{8.24}$$

The radial functions has the properties

- The *Laguerre polynomial* is of the power $(n-\ell-1)$ (see (8.12) and has $(n-\ell-1)$ radial nodes (without $r=0$).
- The probability $P_{n\ell}(r) = r^2|R_{n\ell}^2|$ has $(n-\ell)$ maxima.
- For $(\ell = n-1)$ the radial functions $P_{n,n-1}(r) \propto r^{2n} e^{-\frac{2Zr}{na_0}}$ show only one maximum at $r_{max} = \frac{n^2 a_0}{Z}$.

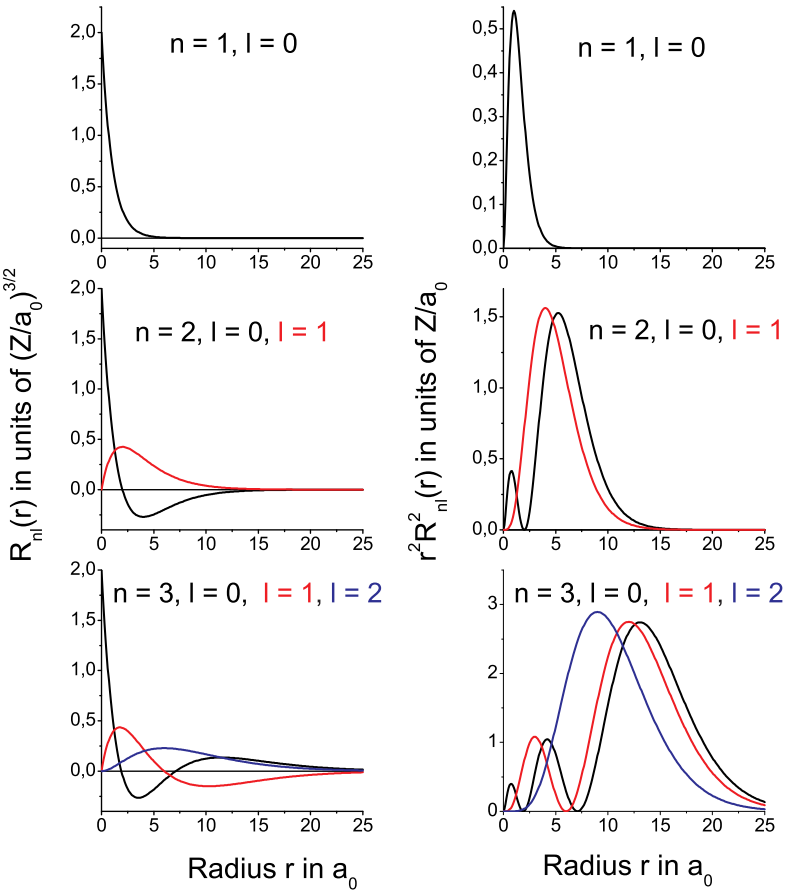


Abbildung 8.2. Radial functions $R_{n\ell}(r)$ and the probability $r^2 R^2_{n\ell}(r)$ of finding an electron in $(r + \Delta r) - r$.

- For a given n the *orbital angular momentum quantum numbers* ℓ can only range from $\{0, 1, \ldots, (n-1)\}$ (see 8.12) and for a given ℓ there are $(2\ell+1)$ *magnetic quantum numbers* m. E_n does not depend on ℓ and m, which is a consequence of the symmetry of $V(r) = -\frac{1}{r}$ and the independence of $R_{n\ell}(r)$ of m, respectively.

- The degeneracy is given by

$$\sum_{\ell=0}^{n-1}(2\ell + 1) = n^2 \tag{8.25}$$

- The expectation value for r, $\langle r \rangle$ is

$$\langle r^k \rangle_{n\ell m} = \int_0^\infty r^k R_{n\ell}^2(r) r^2 \, dr \tag{8.26}$$

$$\langle r \rangle_{n\ell m} = \frac{a_0}{2Z}[3n^2 - \ell(\ell+1)] \tag{8.27}$$

- For $r \to 0$ the radial functions are $R_{n\ell}(r) \propto r^\ell$. For a given n larger values of $R_{n\ell}(r)$ occur for smaller ℓ at a given r (see Fig. 8.2).

- Only radial functions $R_{n\ell}(r)$ with $\ell = 0$ (s-orbitals) are non zero at $r = 0$. This is important for the Mössbauer effect where the orbital overlap of the electronic wave function with the nucleus is responsible for the signal. $|\psi_{n00}|^2 = \frac{1}{4\pi}|R_{n0}(0)|^2 = \frac{Z^3}{\pi n^3 a_0^3}$

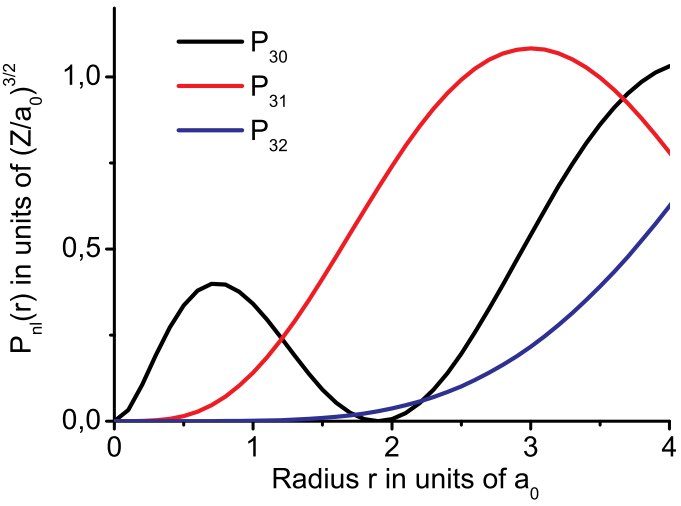


Abbildung 8.3. Probability $r^2 R_{n\ell}^2(r)$ of finding an electron in $(r + \Delta r) - r$ for very small r.

8.3 Hydrogen atom wave functions

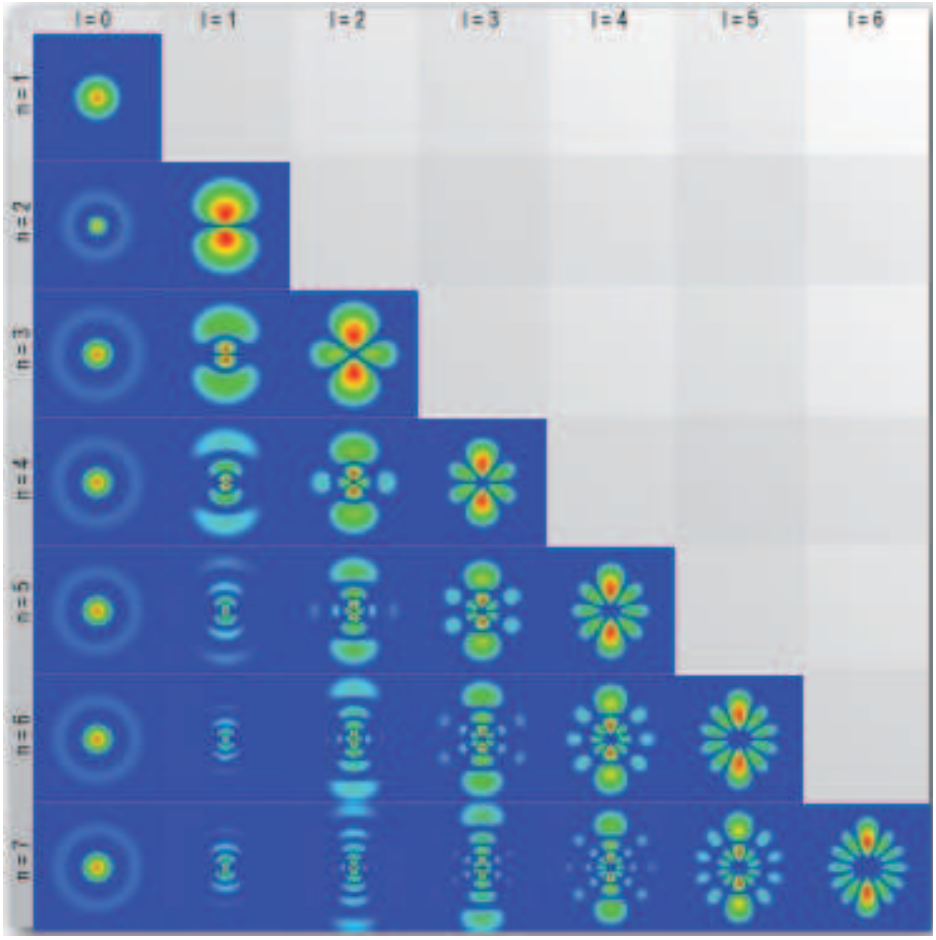


Abbildung 8.4. First wave functions of the hydrogen atom (and similar atomic ions) with $m = 0$.

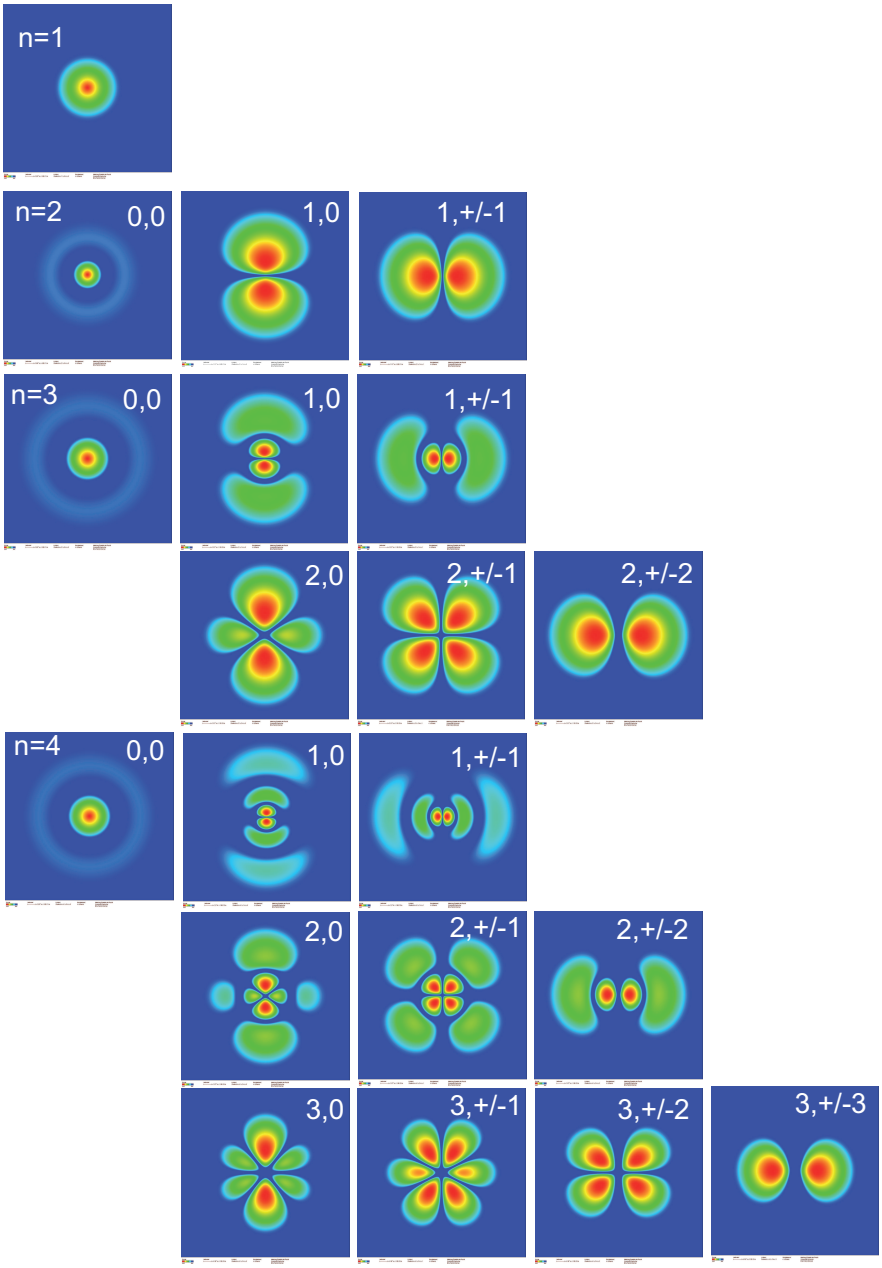


Abbildung 8.5. First wave functions of the hydrogen atom (and similar atomic ions), inserted: quantum numbers.

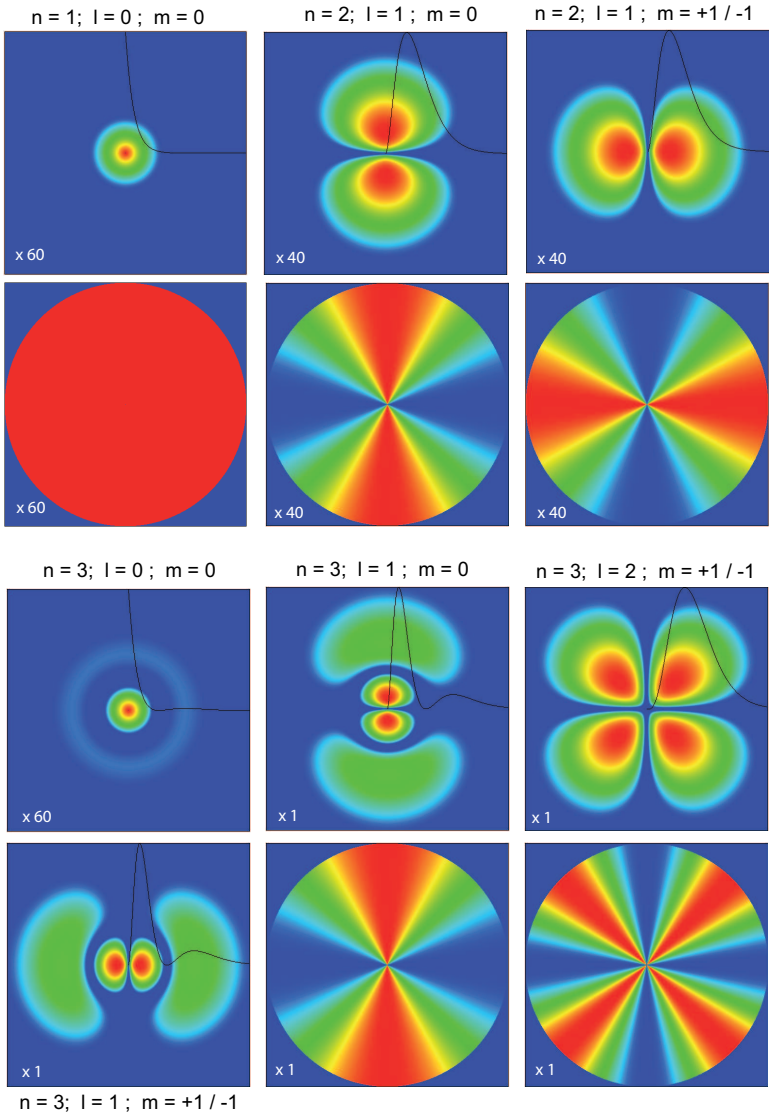


Abbildung 8.6. Some wave functions of the hydrogen atom (and similar atomic ions) plotted together with the quantum numbers. The solid black line represents the radial function, the plots with a fixed radius the spherical harmonics.

8.4 Angular momentum

The functions $Y_{\ell m}(\vartheta, \varphi)$ are simultaneously eigenfunctions of $\overrightarrow{L}^2$ and L_z with eigenvalues $\ell(\ell+1)\hbar^2$ and $m\hbar$, respectively. The angular momentum value $\sqrt{\ell(\ell+1)}\hbar > \ell\hbar$ is always greater than the maximum eigenvalue of $L_z = \ell\hbar$. This means the direction of the vector $\overrightarrow{L}$ is never parallel to the z-axis. Moreover, the $Y_{\ell m}(\vartheta, \varphi)$ are no eigenfunctions of $\langle L_x \rangle$ and $\langle L_y \rangle$ and it is

$$\langle Y_{\ell m}|L_x Y_{\ell m}\rangle = \langle Y_{\ell m}|L_y Y_{\ell m}\rangle = 0 \tag{8.28}$$

$$\langle Y_{\ell m}|L_x^2 Y_{\ell m}\rangle = \langle Y_{\ell m}|L_y^2 Y_{\ell m}\rangle = \frac{1}{2}[\ell(\ell+1) - m^2]\hbar^2. \tag{8.29}$$

We note that the expectation values vanish, but the squares do not vanish (for $\ell \neq 0$). The angular momentum $\overrightarrow{L}$ 'precesses' around the z-axis in the presence of a magnetic field with its projection on the z-axis to be $\hbar m$ and its length $\hbar\sqrt{\ell(\ell+1)}$ (Fig. 8.4). With increasing ℓ and $m = l$ the relative difference between

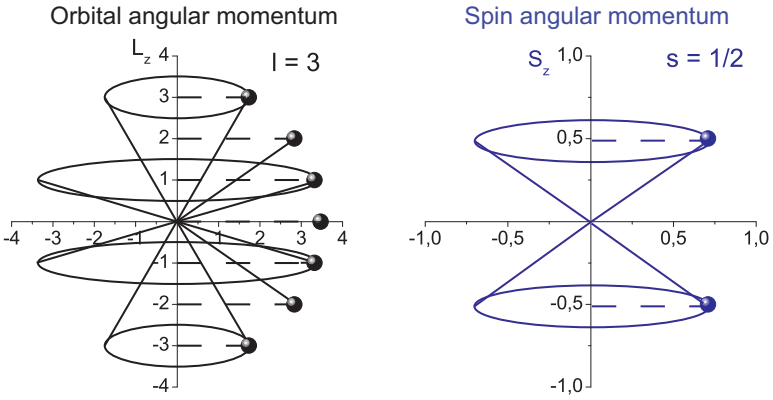


Abbildung 8.7. Projections of the orbital angular momentum and spin angular momentum on the z-axis.

$\sqrt{\ell(\ell+1)}$ and ℓ becomes smaller approximating the classical case, where the angular momentum is parallel to the z-axis and the particle moves in the x-y plane.

The summation over all absolute squared spherical harmonics for a given orbital angular momentum quantum number ℓ results in a value independent of ϑ and φ

$$\sum_{-\ell}^{\ell} |Y_{\ell m}(\vartheta, \varphi)|^2 = \frac{2\ell+1}{4\pi}. \tag{8.30}$$

This means that addition of all $2\ell + 1$ functions $|Y_{\ell m}|^2$ leads to an isotropic function. Since the radial eigenfunctions depend only of n and ℓ, the charge distribution of a filled or closed shell (ℓ-shell) has radial symmetry.

8.5 Spin angular momentum

Electrons possess an intrinsic degree of freedom, the *spin*, which behaves like an angular momentum in the way it couples with a magnetic field (see Stern-Gerlach experiment). The z component of this spin angular momentum can only take on two values $m_s\hbar$, where $m_s = \pm\frac{1}{2}$. Therefore, the electron spin cannot be described by the orbital angular momentum operator $\overrightarrow{L}$, since the z component of $\overrightarrow{L}$ only takes on the values $m\hbar$, with $m = -\ell, -\ell+1, \ldots, \ell$ and $\ell = 0, 1, 2, \ldots$. We assume that all angular momentum operators, whether orbital or spin, satisfy commutation relations of the form (7.107). Thus, if S_x, S_y and S_z are the three Cartesian components of the electron spin angular momentum operator $\overrightarrow{S}$, they must satisfy the commutation relations

$$i\hbar S_z = [S_x, S_y] \tag{8.31}$$
$$i\hbar S_x = [S_y, S_z] \tag{8.32}$$
$$i\hbar S_y = [S_z, S_x]. \tag{8.33}$$

The properties of the spin angular momentum and the simultaneous spin eigenfunctions χ_{s,m_s} of $\overrightarrow{S}^2$ and S_z are

$$\overrightarrow{S}^2\chi_{s,m_s} = s(s+1)\hbar^2\chi_{s,m_s} \tag{8.34}$$
$$S_z\chi_{s,m_s} = m_s\hbar\chi_{s,m_s}. \tag{8.35}$$

Since $m_s = \pm\frac{1}{2}$ for an electron we must have $s = \frac{1}{2}$, and we say the electron spin is one-half. There are two different normalized spin eigenfunctions χ_{s,m_s}, namely

$$\alpha = \chi_{1/2,1/2} \quad \beta = \chi_{1/2,-1/2}. \tag{8.36}$$

Using these equations we get

$$\overrightarrow{S}^2\alpha = \frac{3}{4}\hbar^2\alpha \tag{8.37}$$
$$\overrightarrow{S}^2\beta = \frac{3}{4}\hbar^2\beta \tag{8.38}$$
$$S_z\alpha = \frac{\hbar}{2}\alpha \tag{8.39}$$
$$S_z\beta = -\frac{\hbar}{2}\beta \tag{8.40}$$

The spin eigenfunctions α and β are said to correspond respectively to the spin up ($\uparrow$) and spin down ($\downarrow$) states. General spin-1/2 functions χ are linear superpositions of the spin states α and β. That is

$$\chi = \chi_+\alpha + \chi_-\beta \tag{8.41}$$

where χ_+ and χ_- are the complex coefficients and $|\chi_\pm|^2$ the probability of finding an electron in the 'spin up' (+) α or 'spin down' (-) β state. Some important properties are

$$\begin{aligned}
\langle\chi|\chi\rangle &= 1 && (8.42)\\
|\chi_+|^2 + |\chi_-|^2 &= 1 && (8.43)\\
\langle\alpha|\alpha\rangle &= \langle\beta|\beta\rangle = 1 && (8.44)\\
\langle\beta|\alpha\rangle &= \langle\beta|\alpha\rangle = 0 && (8.45)\\
\overrightarrow{S}^2 &= \frac{3}{4}\hbar^2 && (8.46)\\
S_\pm &= S_x \pm iS_y && (8.47)\\
S_+\alpha &= S_-\beta = 0 && (8.48)\\
S_-\alpha &= \hbar\beta && (8.49)\\
S_+\beta &= \hbar\alpha && (8.50)\\
S_x\alpha &= \frac{\hbar}{2}\beta && (8.51)\\
S_x\beta &= \frac{\hbar}{2}\alpha && (8.52)\\
S_y\alpha &= \frac{i\hbar}{2}\beta && (8.53)\\
S_y\beta &= -\frac{i\hbar}{2}\alpha && (8.54)\\
S_z\alpha &= \frac{\hbar}{2}\alpha && (8.55)\\
S_x\beta &= \frac{\hbar}{2}\beta && (8.56)\\
S_x^2 = S_y^2 = S_z^2 &= \frac{\hbar^2}{4} && (8.57)
\end{aligned}$$

Since there are only two basic spin eigenfunctions α and β, they exist in a two-dimensional 'spin space'. The normalized spin 1/2 eigenfunctions α and β can be considered as basis vectors given by two-component column vectors (also called

spinors)

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{8.58}$$

$$\alpha^\dagger \alpha = \beta^\dagger \beta = 1 \tag{8.59}$$

$$\alpha^\dagger \beta = \beta^\dagger \alpha = 0 \tag{8.60}$$

$$\overrightarrow{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{8.61}$$

$$S_z = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{8.62}$$

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \tag{8.63}$$

$$S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{8.64}$$

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{8.65}$$

$$S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{8.66}$$

The matrices can also be defined by $S_i = \frac{\hbar}{2}\sigma_i$, where the matrices σ_i are called the *Pauli spin matrices*. Using the explicit form (8.58) of the basic spinor α and β, an arbitary spin-1/2 function may be written as the spinor

$$\chi = \begin{pmatrix} \chi_+ \\ \chi_- \end{pmatrix}; \quad \chi^\dagger = (\chi_+^* \quad \chi_-^*). \tag{8.67}$$

It is worth noting that if the electron is in a pure 'spin up' state α or 'spin down' state β, the expectation values of $\langle S_x^2 \rangle$ and $\langle S_y^2 \rangle$ do not vanish (see vector model Fig. 8.4). The quantum number m_s can take on $2s+1$ values $\{-s, -s+1, \ldots, s-1, s\}$.

8.6 Total angular momentum

The total angular momentum can be written as

$$\overrightarrow{J} = \overrightarrow{L} + \overrightarrow{S} \tag{8.68}$$

The orbital angular momentum $\overrightarrow{L} = \overrightarrow{r} \times \overrightarrow{p}$ operates only in 'ordinary' space and satisfies the commutation relations (7.107). On the other hand the spin angular momentum $\overrightarrow{S}$ satisfies the commutation relations (8.33) and operates only in the 'spin space'. All its components therefore commute with those of $\overrightarrow{r}$ and $\overrightarrow{p}$, and

hence with all those of $\overrightarrow{L}$. As a result, the total angular momentum $\overrightarrow{J}$ satisfies the commutation relations

$$i\hbar J_k = [J_i, J_j] \quad \text{with } \{i,j,k\} \text{ cyclic permutating.} \tag{8.69}$$

This characterizes an angular momentum operator $\overrightarrow{J}$ satisfying the eigenvalue equations

$$\overrightarrow{J}^2 \psi_{jm_j} = j(j+1)\hbar^2 \psi_{jm_j} \tag{8.70}$$

$$J_z \psi_{jm_j} = m_j \hbar \psi_{jm_j} \tag{8.71}$$

where j is an integer (including zero) or a half-odd integer ($j = 0, \frac{1}{2}, \frac{3}{2}, \ldots$) and $m_j = -j, -j+1, \ldots, j-1, j$. Since all the components of $\overrightarrow{L}$ commute with all those of $\overrightarrow{S}$, the operators $\overrightarrow{L}^2$, L_z, $\overrightarrow{S}^2$, and S_z mutually commute, and have simultaneous eigenfunctions

$$\psi_{\ell s m_\ell m_s} = Y_{\ell m_\ell}(\vartheta, \varphi) \chi_{s m_s}. \tag{8.72}$$

The simultaneous eigenfunctions of $\overrightarrow{L}^2$, $\overrightarrow{S}^2$, $\overrightarrow{J}^2$ and J_z are linear combinations of the functions $\psi_{\ell s m_\ell m_s}$. For a given value of ℓ and s the possible values of j are given by $j = \{|\ell - s|, |\ell - s| + 1, \ldots, \ell + s\}$ and the quantum number m_j can take on $2j+1$ values (see above).

In general, the wave functions depend on the radial coordinate, the angular momentum, the spin and on the time t. For example, in the case of a spin-1/2 particle (for example, an electron), a general expression for the wave function is

$$\Psi(q,t) = \Psi_+(\overrightarrow{r}, t)\alpha + \Psi_-(\overrightarrow{r}, t)\beta = \begin{pmatrix} \Psi_+ \\ \Psi_- \end{pmatrix} \tag{8.73}$$

where q denotes the ensemble of the continuous spatial variable $\overrightarrow{r}$ and the discrete spin variable ($m_s = \pm\frac{1}{2}$) of the particle. The probability density for finding at time t the particle at $\overrightarrow{r}$ with 'spin up' is $|\Psi_+(\overrightarrow{r}, t)|^2$ (and for 'spin down' $|\Psi_-(\overrightarrow{r}, t)|^2$).

9 Interaction of atoms with electromagnetic radiation

The electromagnetic field $\vec{E}$ and magnetic field $\vec{B}$ can be generated from scalar and vector potentials ϕ and $\vec{A}$ by

$$\vec{E}(\vec{r},t) = -\vec{\nabla}\phi(\vec{r},t) - \frac{\partial}{\partial t}\vec{A}(\vec{r},t) \tag{9.1}$$

$$\vec{B}(\vec{r},t) = \vec{\nabla} \times \vec{A}(\vec{r},t). \tag{9.2}$$

The potentials are not completely defined by (9.1, 9.2), since the fields $\vec{E}$ and $\vec{B}$ are invariant under the (classical) *gauge transformations* $\vec{A} \to \vec{A} + \vec{\nabla}\Theta$ and $\Phi \to \Phi - \frac{\partial \Theta}{\partial t}$, where Θ is any real, differentiable function of $\vec{r}$ and t. The freedom implied by this *gauge invariance* allows us to choose

$$\vec{\nabla} \cdot \vec{A} = 0, \qquad \textit{Coulomb gauge} \tag{9.3}$$

$$\vec{\nabla} \cdot \vec{A} + \frac{\partial \Phi}{\partial t} = 0, \qquad \textit{Lorentz gauge.} \tag{9.4}$$

Using the Coulomb gauge is convenient when no sources are present and therefore $\varrho(t) = \varrho$. When $\vec{A}$ satisfies the Coulomb gauge, one may take $\Phi = 0$, and $\vec{A}$ satisfies the wave equation

$$0 = \vec{\nabla}^2\vec{A} - \frac{1}{c_0^2}\frac{\partial \vec{A}^2}{\partial t^2} \tag{9.5}$$

$$\vec{A}(\vec{r},t) = 2\,A_0(\omega)\,\hat{\varepsilon}\,\cos(\vec{k}\cdot\vec{r} - \omega t + \varphi) \tag{9.6}$$

$$\vec{A}(\vec{r},t) = A_0(\omega)\,\hat{\varepsilon}\,\left[e^{i(\vec{k}\cdot\vec{r}-\omega t+\varphi)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t+\varphi)}\right] \tag{9.7}$$

$$0 = \vec{\nabla}\cdot\vec{A} \quad \Rightarrow \hat{\varepsilon}\cdot\vec{k} = 0, \quad \text{wave is transverse} \tag{9.8}$$

$$\vec{B}(\vec{r},t) = E_0(\omega)\frac{\vec{k}\times\hat{\varepsilon}}{\omega}\sin(\vec{k}\cdot\vec{r} - \omega t + \varphi), \text{ with } E_0(\omega) = \omega A_0(\omega) \tag{9.9}$$

$$\text{Energy density} : \frac{1}{2}(\varepsilon_0|E|^2 + \frac{|B|^2}{\mu_0}) = \varepsilon_0 E_0^2 \sin^2(\vec{k}\cdot\vec{r} - \omega t + \varphi) \tag{9.10}$$

$$I(\omega) = \rho(\omega)c_0 = \frac{1}{2}\varepsilon_0 c_0 E_0^2(\omega) = \hbar\omega N(\omega)\frac{c_0}{V} \tag{9.11}$$

$$\vec{A}(\vec{r},t) = \hat{\varepsilon}\int_{-\infty}^{\infty} A_0(\omega)e^{i(\vec{k}\cdot\vec{r}-\omega t+\varphi)}d\omega \tag{9.12}$$

$$\vec{A}(\vec{r},t) = \hat{\varepsilon}\int_{0}^{\infty} A_0(\omega)\cos(\vec{k}\cdot\vec{r} - \omega t + \varphi)d\omega \tag{9.13}$$

Here, φ is a random phase and for a given fixed direction of $\widehat{\varepsilon}$ the electromagnetic field is linear polarized.

The Hamiltonian of a spinless particle of charge q and mass m in an electromagnetic field is

$$H = \frac{1}{2m}(\overrightarrow{p} - q\overrightarrow{A})^2 + q\Phi \tag{9.14}$$

Ignoring small spin-dependent terms the time-dependent SE is

$$\left[\frac{1}{2m}\left(\frac{\hbar}{i}\overrightarrow{\nabla} + e\overrightarrow{A}(\overrightarrow{r},t)\right)^2 + e\Phi(\overrightarrow{r},t) - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]\psi(\overrightarrow{r},t) = i\hbar\frac{\partial\psi(\overrightarrow{r},t)}{\partial t} \tag{9.15}$$

Assuming time independent fields $\overrightarrow{A}(\overrightarrow{r},t) = \overrightarrow{A}(\overrightarrow{r})$ and $\Phi = \Phi(\overrightarrow{r})$ the Hamilton operator becomes time independent and the wave function is

$$\psi(\overrightarrow{r},t) = e^{-i\frac{Et}{\hbar}}\psi(\overrightarrow{r}) \tag{9.16}$$

and the SE becomes with $\overrightarrow{\nabla}\cdot(\overrightarrow{A}\psi) = (\overrightarrow{\nabla}\cdot\overrightarrow{A})\psi + \overrightarrow{A}\cdot\overrightarrow{\nabla}\psi$

$$\left[-\frac{\hbar^2}{2m}\triangle - \frac{i\hbar e}{m}\overrightarrow{A}\cdot\overrightarrow{\nabla} - \frac{i\hbar e}{2m}\underbrace{\overrightarrow{\nabla}\cdot\overrightarrow{A}}_{=0} + \frac{e^2}{2m}(\overrightarrow{A}\cdot\overrightarrow{A}) - \frac{Ze^2}{4\pi\varepsilon_0 r} + e\Phi(\overrightarrow{r})\right]\psi = E\psi$$

$$\overset{\Phi=0}{\Rightarrow}\left[-\frac{\hbar^2}{2m}\triangle - \frac{i\hbar e}{m}\overrightarrow{A}\cdot\overrightarrow{\nabla} + \frac{e^2}{2m}(\overrightarrow{A}\cdot\overrightarrow{A}) - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]\psi = E\psi \tag{9.17}$$

In a constant magnetic field we can write

$$\overrightarrow{A} = \frac{1}{2}(\overrightarrow{B}\times\overrightarrow{r}) \tag{9.18}$$

$$-\frac{i\hbar e}{m}\overrightarrow{A}\cdot\overrightarrow{\nabla} = -\frac{i\hbar e}{2m}(\overrightarrow{B}\times\overrightarrow{r})\cdot\overrightarrow{\nabla} \tag{9.19}$$

$$= -\frac{i\hbar e}{2m}\overrightarrow{B}\cdot(\overrightarrow{r}\times\overrightarrow{\nabla}) = \frac{e}{2m}\overrightarrow{B}\cdot\overrightarrow{L}. \tag{9.20}$$

Here we used the definition $\overrightarrow{L} = \overrightarrow{r}\times\overrightarrow{p} = -i\hbar\overrightarrow{r}\times\overrightarrow{\nabla}$ of the orbital angular momentum operator. The quadratic term $\overrightarrow{A}\cdot\overrightarrow{A}$ is

$$\frac{e^2\overrightarrow{A}\cdot\overrightarrow{A}}{2m} = \frac{e^2(\overrightarrow{B}\times\overrightarrow{r})^2}{8m} \tag{9.21}$$

$$= \frac{e^2}{8m}(B^2r^2 - (\overrightarrow{B}\cdot\overrightarrow{r})^2) \overset{\overrightarrow{B}=B_z}{=} \frac{e^2B^2}{8m}(x^2+y^2) \tag{9.22}$$

Here we choose the axis of the magnetic field to be parallel to the z-axis. If we compare the terms linear and quadratic in $\overrightarrow{A}$ we find

$$\frac{e}{2m}\overrightarrow{B}\cdot\overrightarrow{L} \approx \frac{e\hbar}{2m}B, \quad (1) \tag{9.23}$$

$$\frac{e^2B^2}{8m}(x^2+y^2) \approx \frac{e^2B^2}{4m}a_0^2, \quad (2) \tag{9.24}$$

$$\Rightarrow \frac{(2)}{(1)} = \frac{ea_0^2B}{2\hbar} \approx 10^{-6}B, \quad \text{with B in T} \tag{9.25}$$

Therefore, the second term is negligible and term (1) describes the potential energy of a magnetic dipole moment $\overrightarrow{\mu}$ in a magnetic field $\overrightarrow{B}$. The magnetic dipole moment $\overrightarrow{\mu}$ is defined by

$$\overrightarrow{\mu} = -\frac{e}{2m}\overrightarrow{L} = -\mu_B\frac{\overrightarrow{L}}{\hbar}. \tag{9.26}$$

With *Bohr's magneton* μ_B:

$$\mu_B = \frac{e\hbar}{2m} \approx 9.27408\times10^{-24}\ \text{Am}^2, \quad \text{(Joule/Tesla)}. \tag{9.27}$$

Now we define this small interaction to be a perturbation H' to the system

$$H' = -\overrightarrow{B}\cdot\overrightarrow{\mu} \approx 0.4669\overrightarrow{B}\cdot\frac{\overrightarrow{L}}{\hbar}\ \text{cm}^{-1}, \quad \text{B in Tesla} \tag{9.28}$$

and the SE becomes

$$\left[-\frac{\hbar^2}{2m}\triangle - \frac{Ze^2}{4\pi\varepsilon_0 r} + H'\right]\psi = E\psi. \tag{9.29}$$

For $H' = 0$ we know the eigenfunctions $\psi_{n\ell m_\ell}$ of the hydrogen atom, that are also eigenfunctions of $\overrightarrow{L}^2$ and L_z. If we choose the magnetic field parallel to the z-axis we have

$$H' = \frac{e}{2m}BL_z. \tag{9.30}$$

With this setting the SE is readily solved without perturbation theory, since the eigenfunctions $\psi_{n\ell m_\ell}$ are eigenfunctions of the perturbation L_z also

$$E_{nm_\ell} = -\frac{mZ^2e^4}{2\hbar^2(4\pi\varepsilon_0)^2n^2} + \frac{eB}{2m}\hbar m_\ell = -\frac{mZ^2e^4}{2\hbar^2(4\pi\varepsilon_0)^2n^2} + \hbar\omega_L m_\ell. \tag{9.31}$$

The magnetic quantum numbers can take on values $-\ell,\ldots,\ell$, and ω_L is called Larmor frequency.

$$\omega_L = \frac{eB}{2m} \tag{9.32}$$

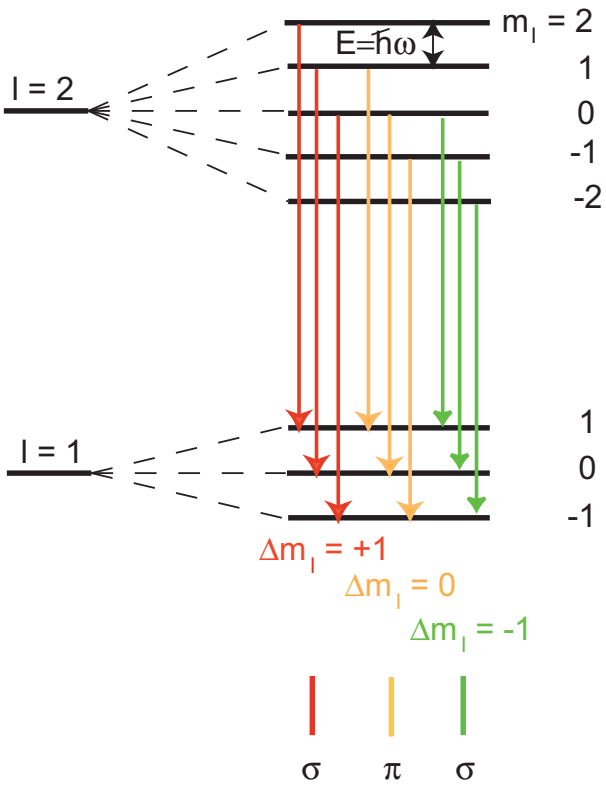


Abbildung 9.1. In the presence of a magnetic field the $2\ell + 1$ states are not degenerate any more. The energy spacing is $\Delta E = \frac{eB\hbar}{2m}$ and the transitions are connected to different polarizations for π and σ.

We observe a term splitting for the $2\ell + 1$ terms, that are no longer degenerate. Note, only in hydrogen atoms the degeneracy of states with the same n and m_ℓ is still valid. For a magnetic field of 1 Tesla (Lab magnet) the splitting is approximately 9.27×10^{-24} J $\approx 0.58 \times 10^{-4}$eV, which is small compared to the ground state energy of the hydrogen atom (13.6 eV). Possible transitions between the energy levels obey selection rules. Selection rules state which transitions are allowed (other transitions are forbidden). Here, the selection rules are

$$\Delta m_\ell = 0 \quad (\pi) \tag{9.33}$$

$$\Delta m_\ell = \pm 1 \quad (\sigma). \tag{9.34}$$

Thus, three transitions are allowed. They are called *Lorentz triplet* (1896). They were observed in an experiment called the normal Zeeman effect that is shown in Fig. 9. Moreover, the number of observable transitions depend on the direction of observation. For observation directions perpendicular to the magnetic field, three optical transitions are detectable with linear polarizations along the z-axis (π) and the y-axis (σ). Detection along the z-axis (longitudinal) result in two optical transitions absorbing circular polarized light (σ^- and σ^+).

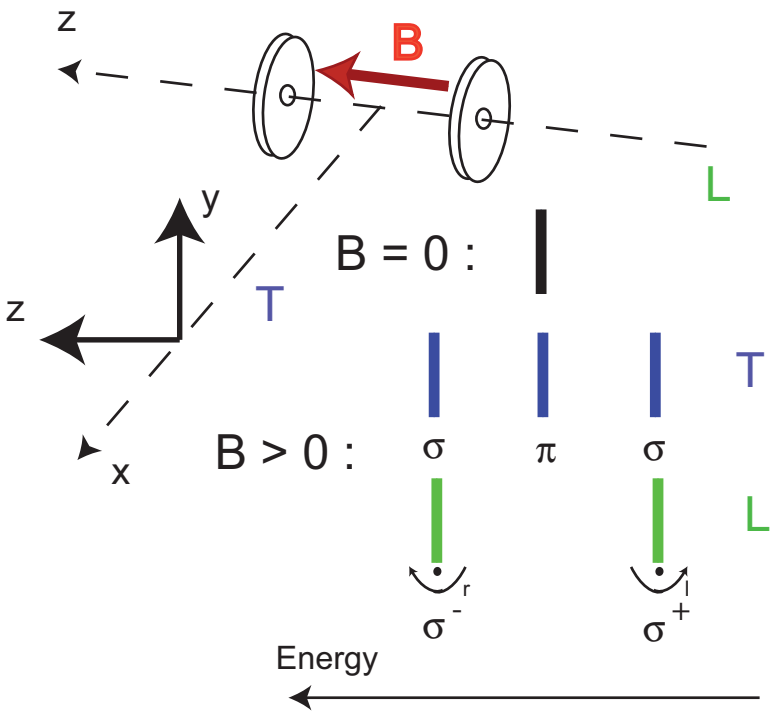


Abbildung 9.2. Normal Zeeman effect: If no magnetic field ($B = 0$) is applied to the set-up, only a single absorption line is observed along the z-axis (L) and x-axis (T). When a constant magnetic field is directed along the z-axis, two absorption signals are observed along the longitudinal direction (L) and three absorption signals along the transversal direction (T). The polarization of the absorbed fields are circular (σ^- and σ^+) for the longitudinal direction and parallel (π and σ) along the transversal direction. The energy splitting between the three levels is $\frac{e\hbar B}{2m}$ each.

If we would take into account the additional interaction of the spin with the magnetic moment $\overrightarrow{\mu_s}$

$$\overrightarrow{\mu_s} = -g_s \mu_B \frac{\overrightarrow{S}}{\hbar} \tag{9.35}$$

we would find an additional term in the SE with $-\overrightarrow{B} \cdot \overrightarrow{\mu_s}$. In such experiments with a weak magnetic field the $\overrightarrow{L} \cdot \overrightarrow{S}$ coupling introduces an additional term into the SE leading to the *anomalous Zeeman effect*. For $|\overrightarrow{S}| = 0$ the normal Zeeman effect will be observed.

The transitions between specific energy levels are due to the interaction of the atoms with the electromagnetic field. Since, the electromagnetic field is described by a time-dependent vector potential $\overrightarrow{A}(t)$ the perturbation H' is no longer time-

independent and the SE becomes

$$[H_0 + \lambda H'(t)]\,\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{9.36}$$

9.1 Time-dependent perturbation theory

The time-dependent perturbation theory is used for situations where the perturbation to the system $\lambda H'(t)$ is small and time dependent. The unperturbed system has the eigenfunctions $\{\psi_n\}$ of the SE $H_0\psi_n = E_n^0\psi_n$. The perturbation is time-dependent and in our case given by

$$\lambda H'(t) = -i\frac{\hbar e}{m}\overrightarrow{A}(t)\cdot\overrightarrow{\nabla} \tag{9.37}$$

$$= -i\frac{\hbar e}{m}\overrightarrow{A}_0\left[e^{i(\overrightarrow{k}\cdot\overrightarrow{r}-\omega t)} + e^{-i(\overrightarrow{k}\cdot\overrightarrow{r}-\omega t)}\right]\cdot\overrightarrow{\nabla} \tag{9.38}$$

Since the eigenfunctions $\{\psi_n\}$ are orthonormal and define a complete set, the general solution $\psi(\overrightarrow{r},t)$ of

$$[H_0 + \lambda H'(t)]\,\psi(\overrightarrow{r},t) = i\hbar\frac{\partial\psi(\overrightarrow{r},t)}{\partial t} \tag{9.39}$$

can be expanded by

$$\psi(\overrightarrow{r},t) = \sum_n c_n(t)e^{-iE_n^{(0)}t/\hbar}\psi_n(\overrightarrow{r}) \tag{9.40}$$

where $c_n(t)$ are time-dependent coefficients describing the amplitude changes changes of the eigenfunctions with time. To find the coefficients, equation (9.40) is inserted into the SE (9.39), and we have

$$\sum_n c_n(t)e^{-iE_n^{(0)}t/\hbar}\left[\underline{H_0\psi_n} + \lambda H'(t)\psi_n\right] = i\hbar\sum_n\left(\frac{dc_n}{dt}e^{-iE_n^{(0)}t/\hbar}\psi_n - \underline{\frac{iE_n^0}{\hbar}c_n(t)e^{-iE_n^{(0)}t/\hbar}\psi_n}\right) \tag{9.41}$$

$$\lambda\sum_n c_n(t)H'(t)e^{-iE_n^{(0)}t/\hbar}\psi_n = i\hbar\sum_n\frac{dc_n}{dt}e^{-iE_n^{(0)}t/\hbar}\psi_n \tag{9.42}$$

$$\overset{\int\psi^*[\ldots]}{\Rightarrow}\ \lambda\sum_n c_n(t)e^{-iE_n^{(0)}t/\hbar}\langle\psi_m|H'(t)\psi_n\rangle = i\hbar\frac{dc_m}{dt}e^{-iE_m^{(0)}t/\hbar} \tag{9.43}$$

$$\overset{\omega_{mn}=\frac{E_m^0-E_n^0}{\hbar}}{\Rightarrow}\qquad i\hbar\frac{dc_m}{dt} = \lambda\sum_n c_n(t)e^{i\omega_{mn}t}H'_{mn}(t) \tag{9.44}$$

The system of coupled differential equations (9.44) is completely equivalent to the original SE $i\hbar\frac{\partial\psi(\overrightarrow{r},t)}{\partial t} = H\psi(\overrightarrow{r},t)$, and no approximations has been made thus

far. However, if the perturbation $\lambda H'$ is weak, we can expand the coefficients c_n and c_m in powers of the parameter λ as

$$c_n(t) = c_n^{(0)}(t) + \lambda c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \dots . \tag{9.45}$$

Substituting this expansion into the system (9.44) and equating the coefficients of equal powers of λ, we find that

$$\begin{aligned}
\dot{c}_m^{(0)} &= 0 && (9.46)\\
\dot{c}_m^{(1)} &= \frac{1}{i\hbar}\sum_n c_n^{(0)}(t) H'_{mn}(t) e^{i\omega_{mn}t} && (9.47)\\
\dot{c}_m^{(2)} &= \frac{1}{i\hbar}\sum_n c_n^{(1)}(t) H'_{mn}(t) e^{i\omega_{mn}t} && (9.48)\\
&\vdots \qquad\qquad \vdots\\
\dot{c}_m^{(s+1)} &= \frac{1}{i\hbar}\sum_n c_n^{(s)}(t) H'_{mn}(t) e^{i\omega_{mn}t} && (9.49)
\end{aligned}$$

Thus, the original system (9.44) has been decoupled in such a way that the equations can now in principle be integrated successively to any given order. The first equation (9.46) simply confirms that the coefficients $c_m^{(0)}$ are time-independent. Since we want to describe transitions from an initial state ψ_i to a final state ψ_f, we assume that for $t \le t_0$ the system is in the initial state $\psi(t \le t_0) = \psi_i$ with energy E_i^0 and the perturbation $H'(t)$ is switched on at time $t_0 = 0$. The probability of finding the system in the state m is $|c_m(t)|^2$

$$\begin{aligned}
\Rightarrow \frac{dc_m^{(1)}}{dt} &= \frac{1}{i\hbar} e^{i\omega_{mi}t} H'_{mi}(t) && (9.50)\\
c_i^{(1)}(t) &= c_i^{(1)}(t_0) + \frac{1}{i\hbar}\int_{t_0}^{t} H'_{ii}(t')dt' && (9.51)\\
c_m^{(1)}(t) &= c_m^{(1)}(t_0) + \frac{1}{i\hbar}\int_{t_0}^{t} e^{i\omega_{mi}t'} H'_{mi}(t')dt' && (9.52)
\end{aligned}$$

where the integration constants in (9.52 and 9.51) has be chosen in such a way that $c_m^{(1)}(t) = c_i^{(1)}(t)$ vanish at $t = t_0$, before the perturbation is applied. To first order in the perturbation, the *transition probability* corresponding to the transition $i \to m$ is therefore given by

$$P_{mi}^{(1)}(t) = |c_m^{(1)}(t)|^2 = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} H'_{mi}(t) e^{i\omega_{mi}t'} dt'\right|^2, \quad i \neq m \tag{9.53}$$

The coefficient c_i of the state i is given to first order in perturbation by

$$c_i(t) = c_i^{(0)} + c_i^{(1)}(t) \tag{9.54}$$

$$\approx 1 + \frac{1}{i\hbar}\int_{t_0}^{t} H'_{ii}(t')dt' \tag{9.55}$$

$$\approx e^{-\frac{i}{\hbar}\int_{t_0}^{t} H'_{ii}(t')dt'} \tag{9.56}$$

so that $|c_i(t)|^2 \approx 1$ and the main effect of the perturbation is to change the phase of the initial state.

9.1.1 Time-independent perturbation

If H' is time-independent, except for being switched on suddenly at a given time $t_0 = 0$. We then have

$$c_i^{(1)}(t) = \frac{1}{i\hbar}H'_{ii}t \tag{9.57}$$

$$c_m^{(1)}(t) = \frac{H'_{mi}}{\omega_{mi}\hbar}\left(1 - e^{i\omega_{mi}t}\right), \quad m \neq i \tag{9.58}$$

$$P_{mi}^{(1)}(t) = |c_m^{(1)}(t)|^2 = \frac{2|H'_{mi}|^2}{\hbar^2}F(t,\omega_{mi}) \tag{9.59}$$

$$F(t,\omega_{mi}) = \frac{1-\cos(\omega_{mi}t)}{\omega_{mi}^2} = \frac{2\sin^2(\omega_{mi}t/2)}{\omega_{mi}^2} \tag{9.60}$$

The height of the peak of the function $F(t,\omega)$ is proportional to t^2, while its width is approximately $2\pi/t$. Setting $\omega t/2 = x$ we have

$$\int_{-\infty}^{\infty} F(t,\omega)d\omega = t\int_{-\infty}^{\infty}\frac{\sin^2 x}{x^2}dx = \pi t, \tag{9.61}$$

and for $t \to \infty$ we have $F(t,\omega) \approx \pi t\delta(\omega)$ and for $\omega \to 0$ we have $F(t,\omega) \to \left(\frac{t}{2}\right)^2$. From that we can conclude for the transition probability

- At a fixed time t, $F(t,\omega)$ has a sharp peak of width $2\pi/t$ about the value $\omega_{mi} = 0$. It is clear that transitions to m for which ω_{mi} does not deviate form zero by more than $\delta\omega_{mi} \approx 2\pi/t$ will be strongly favoured. Therefore the transitions $i \to m$ will occur mainly towards those final states m whose energy is located in a band of width $\delta E \approx 2\pi\hbar/t$
- If the transition is such that $\omega_{mi} = 0$, $E_m = E_i$, and the states are degenerate, then the transition probability is given by

$$P_{mi}^{(1)}(t) = \frac{|H'_{mi}|^2}{\hbar^2}t^2 \tag{9.62}$$

and at sufficient length of time the quantity $P_{mi}^{(1)}(t)$ will no longer satisfy the inequality $P_{mi}^{(1)}(t) \ll 1$ required by the perturbation approach. Hence, the perturbation method cannot be applied to degenerate systems which are perturbed over long periods of time.

- If $\omega_{mi} \neq 0$ we have

$$P_{mi}^{(1)}(t) = \frac{4|H'_{mi}|^2}{\hbar^2\omega_{mi}^2}\sin^2(\frac{\omega_{mi}t}{2}) \tag{9.63}$$

and $P_{mi}^{(1)}(t)$ oscillates with a period $2\pi/|\omega_{mi}|$ about the average value $\frac{2|H'_{mi}|^2}{\hbar^2\omega_{mi}^2}$. If the perturbation H' is sufficient weak, the inequality $P_{mi}^{(1)}(t) \ll 1$ can always be satisfied. Note, for times t small with respect to the period of oscillation one has

$$t \text{ small } : \; P_{mi}^{(1)}(t) \approx \frac{4|H'_{mi}|^2}{\hbar^2\omega_{mi}^2}\left(\frac{\omega_{mi}t}{2}\right)^2 \approx |H'_{mi}|^2\frac{t^2}{\hbar^2} \tag{9.64}$$

- If we consider transitions involving a group of states n whose energy E_n lies within $(E_m^{(0)} - \eta, E_m^{(0)} + \eta)$ centered about $E_m^{(0)}$ and we denote $\rho_n(E_n)$ the density of levels on the energy scale, so that $\rho_n(E_n)dE_n$ is the number of final states n in an interval dE_n containing the energy E_n. The first-order transition probability $P_{ni}^{(1)}(t)$ from the initial state i to the group of final states n is then given by

$$P_{ni}^{(1)}(t) = \sum_n |c_n^{(1)}(t)|^2 = \frac{4|H'_{ni}|^2}{\hbar^2}\int_{-\infty}^{\infty}\frac{\sin^2(\frac{\omega_{ni}t}{2})}{\omega_{ni}^2}\rho_n(E_n)\hbar d\omega_n \tag{9.65}$$

$$= \frac{2}{\hbar^2}\int_{E_m^{(0)}-\eta}^{E_m^{(0)}+\eta}|H'_{ni}|^2F(t,\omega_{ni})\rho_n(E_n)dE_n \tag{9.66}$$

$$\approx \frac{2}{\hbar}\rho_n(E_n)|H'_{ni}|^2\int_{-\infty}^{\infty}F(t,\omega_{ni})d\omega_n \tag{9.67}$$

$$= \frac{2\pi}{\hbar}\rho_n(E_n)|H'_{ni}|^2t \tag{9.68}$$

If t is large enough so that $\eta \gg 2\pi\hbar/t$ the dominating part of the integral arises from transitions which conserve the energy (within $\delta E = 2\pi\hbar/t$), and we have

$$P_{ni}^{(1)}(t) = \frac{2\pi}{\hbar}|H'_{ni}|^2\rho_n(E)t \quad \Rightarrow \quad W_{ni} = \frac{2\pi}{\hbar}|H'_{ni}|^2\rho_n(E) \tag{9.69}$$

with W_{ni} is the *transition probability per unit time* or *transition rate*. This is called 'the Golden Rule' of perturbation theory.

9.1.2 Periodic perturbation

Let us now consider a periodic perturbation

$$H'(t) = Ve^{i\omega t} + V^* e^{-i\omega t}. \tag{9.70}$$

With this definition $H'(t)$ is hermitian, and the system is initially (for $t \leq 0$) in the unperturbed bound state $\psi_i^{(0)}$, of energy $E_i^{(0)}$, so that the initial conditions are $c_i(t \leq 0) = 1$ and $c_m(t \leq 0) = 0$ for $m \neq i$. To calculate $c_m(t)$ we substitute (9.70) into (9.52) and use the fact that $t_0 = 0$. This gives

$$\begin{aligned} c_m^{(1)}(t) &= \frac{1}{i\hbar}\left[V_{mi}\int_0^t e^{i(\omega_{mi}+\omega)t'}dt' + V_{mi}^*\int_0^t e^{i(\omega_{mi}-\omega)t'}dt'\right] \\ \overset{\hbar\omega_{mi}=E_m^{(0)}-E_i^{(0)}}{\Rightarrow} \quad P_{mi}^{(1)}(t) &= \left|V_{mi}\frac{1-e^{i(E_m^{(0)}-E_i^{(0)}+\hbar\omega)t/\hbar}}{E_m^{(0)}-E_i^{(0)}+\hbar\omega} + \right. \\ &\quad \left. V_{mi}^*\frac{1-e^{i(E_m^{(0)}-E_i^{(0)}-\hbar\omega)t/\hbar}}{E_m^{(0)}-E_i^{(0)}-\hbar\omega}\right|^2 \end{aligned} \tag{9.71}$$

Only one of the two terms contribute to the transition probability. For $E_m^{(0)} = E_i^{(0)} + \hbar\omega$ the second term will have an appreciable magnitude, and the corresponding transition probability being given by

$$P_{mi}^{(1)}(t) = \frac{2}{\hbar^2}|V_{mi}^*|^2 F(t, \omega_{mi} - \omega). \tag{9.72}$$

The two terms describe the physical processes of

$$\hbar\omega = E_m^{(0)} - E_i^{(0)}, \quad \text{Absorption} \tag{9.73}$$

$$\hbar\omega + E_m^{(0)} = E_i^{(0)}, \quad \text{Emission} \tag{9.74}$$

and for discrete transitions the density of states becomes $\rho_n(E) = \delta(E_m^{(0)} - E_i^{(0)} \mp \hbar\omega)$. The main difference to the time-independent case is that ω_{mi} is replaced by $\omega_{mi} - \omega$. We see that the transition probability will only be significant if $E_m = E_i + \hbar\omega$ and the system has absorbed an amount of energy given by $\hbar\omega$. If we take into account that the electric field is a vector we can write

$$V = -\frac{e}{2}\overrightarrow{E}\cdot\overrightarrow{r} \tag{9.75}$$

$$= -\frac{e}{2}\overrightarrow{E_0}\cdot\overrightarrow{r}\left(e^{i\omega t} + e^{-i\omega t}\right) \tag{9.76}$$

$$H'_{mi}(t) = -\frac{1}{2}\overrightarrow{E_0}\left(e^{i\omega t} + e^{-i\omega t}\right)\langle\psi_m|e\overrightarrow{r}\psi_i\rangle \tag{9.77}$$

$$\overrightarrow{\underline{\mu}}_{mi} = \langle\psi_m|e\overrightarrow{r}\psi_i\rangle \tag{9.78}$$

$$H'_{mi}(t) = -\frac{1}{2}\overrightarrow{E_0}\cdot\overrightarrow{\underline{\mu}}_{mi}\left(e^{i\omega t} + e^{-i\omega t}\right). \tag{9.79}$$

The vector $\overrightarrow{\mu}_{mi}$ is called transition dipole moment for the transition $i \to m$. The coefficient $|c_m^{(1)}(t)|^2$ is given for long times as

$$|c_m^{(1)}(t)|^2 = \frac{1}{\hbar^2}|\overrightarrow{E_0} \cdot \overrightarrow{\underline{\mu}}_{mi}|^2(\pi\delta(\omega+\omega_{mi}) + \pi\delta(\omega-\omega_{mi}))t. \tag{9.80}$$

The energy conservation is fulfilled by the delta functions for absorption and emission. The Probability is given by

$$\begin{aligned} |c_m^{(1)}(t)|^2 &= \left|\frac{\overrightarrow{E_0} \cdot \overrightarrow{\underline{\mu}}_{mi}}{2\hbar}\frac{e^{i(\omega_{mi}-\omega)t}-1}{\omega_{mi}-\omega}\right|^2 && (9.81)\\ &= \frac{|\overrightarrow{E_0} \cdot \overrightarrow{\underline{\mu}}_{mi}|^2}{2\hbar^2}\frac{2\sin^2((\omega_{mi}-\omega)t/2)}{(\omega_{mi}-\omega)^2} && (9.82)\\ &= \frac{|\overrightarrow{E_0}|^2|\overrightarrow{\underline{\mu}}_{mi}|^2}{3\hbar^2}\frac{\sin^2((\omega_{mi}-\omega)t/2)}{(\omega_{mi}-\omega)^2} && (9.83) \end{aligned}$$

Here, we used an isotropic distribution of transition dipole moments. For continuous distribution of states with nearly constant density of states about $\omega_{mi} = \omega$ we have the transition probability integrated over the frequencies

$$\begin{aligned} P_m(t) &= \frac{1}{6\hbar^2}|\overrightarrow{E_0}|^2|\overrightarrow{\underline{\mu}}_{mi}|^2\rho(\omega)\int_{-\infty}^{\infty} F(t,\omega_{mi}-\omega)d\omega && (9.84)\\ &= \frac{\pi}{6\hbar^2}|\overrightarrow{E_0}|^2|\overrightarrow{\underline{\mu}}_{mi}|^2\rho(\omega)t && (9.85) \end{aligned}$$

and we can finally calculate the transition rate

$$W_{mi} = \frac{P_m(t)}{t} = \frac{\pi}{6\hbar^2}|\overrightarrow{E_0}|^2|\overrightarrow{\underline{\mu}}_{mi}|^2\rho(\omega) \tag{9.86}$$

that is constant and given by the transition dipole moment and the strength of the electric field. The transition rates for absorption and emission are equal since the dipole operator $\sum_k e\overrightarrow{r_k}$ is hermitian $\langle\psi_m|e\overrightarrow{r}\psi_i\rangle = \langle\psi_i|e\overrightarrow{r}\psi_m\rangle$.

9.2 Absorption and emission

Using a perturbation of the form

$$H'_{mi}(t) = -i\hbar\frac{e}{m}\overrightarrow{A} \cdot \overrightarrow{\nabla} \tag{9.87}$$

the equation for the coefficient becomes

$$c_m^{(1)}(t) = \frac{1}{i\hbar}\int_0^t \langle\psi_m|\overrightarrow{A} \cdot \overrightarrow{\nabla}\psi_i\rangle e^{i(\omega_{mi})t'}dt'. \tag{9.88}$$

Inserting (9.13) we have

$$c_m^{(1)}(t) = -\frac{e}{2m}\int_0^\infty A_0(\omega)d\omega \left[e^{i\varphi}\langle\psi_m|e^{i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}\psi_i\rangle \int_0^t e^{i(\omega_{mi}-\omega)t'}dt' \right.$$
$$\left. + e^{-i\varphi}\langle\psi_m|e^{-i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}\psi_i\rangle \int_0^t e^{i(\omega_{mi}+\omega)t'}dt' \right]. \quad (9.89)$$

The first term describes absorption, the second one emission. The probability for the system to be in the m state at time t (with initial conditions $|c_m(t \le 0)|^2 = 0$ and $|c_i(t \le 0)|^2 = 1$) is

$$|c_m(t)|^2 = \frac{\pi e^2}{2m^2}A_0^2(\omega_{mi})|M_{mi}(\omega_{mi})|^2 t. \quad (9.90)$$

Thus the probability increases linearly with time and the transition rate for absorption (integrated over ω) can be defined in first-order perturbation theory as

$$W_{mi} = \frac{4\pi^2}{m^2 c_0}\frac{e^2}{4\pi\varepsilon_0}\frac{I(\omega_{mi})}{\omega_{mi}^2}|M_{mi}(\omega_{mi})|^2 \quad (9.91)$$

$$\sigma_{mi} = \frac{4\pi^2\alpha\hbar^2}{m^2\omega_{mi}}|M_{mi}(\omega_{mi})|^2 \quad (9.92)$$

where $\alpha = e^2/(4\pi\varepsilon_0\hbar c_0) \simeq 1/137$ is the fine structure constant. The term σ_{mi} is called the absorption cross-section which is the rate of absorption of energy (per atom) divided by $I(\omega_{mi})$. It has the dimensions area divided by time.

Evaluating the second term gives the transition rate for emission (integrated over ω):

$$\bar{M}_{im} = -M_{mi}^* \quad (9.93)$$

$$\bar{W}_{im} = \frac{4\pi^2}{m^2 c_0}\frac{e^2}{4\pi\varepsilon_0}\frac{I(\omega_{mi})}{\omega_{mi}^2}|\bar{M}_{im}(\omega_{mi})|^2 \quad (9.94)$$

$$\bar{W}_{im} = W_{mi} \quad (9.95)$$

$$\bar{\sigma}_{im} = \sigma_{mi} \quad (9.96)$$

$$B_{mi} = \frac{W_{mi}}{\rho} = \frac{4\pi^2}{3\hbar^2}\frac{1}{4\pi\varepsilon_0}|\sum_n -e\vec{r_n}|^2 \quad (9.97)$$

Here, we see that the absorption rate is the same as the emission rate as found before, and the absorption and emission cross-sections are also the same. This is consistent with the *principle of detailed balancing*, which says that in an enclosure

containing atoms and radiation in equilibrium, the transition from i to f is the same as that from f to i, where f and i are any pair of states. The Einstein coefficients B_{mi} depend on the matrix element M_{mi} which determines the strength of a transition.

9.3 Selection rules

Having neglected the term $\overrightarrow{A}^2$ in the interaction of matter with light, the SE may be written as

$$i\hbar\frac{\partial}{\partial t}\psi(\overrightarrow{r},t) = [H_0 + H'(t)]\psi(\overrightarrow{r},t) \tag{9.98}$$

If we assume a time-dependent perturbation caused by an oscillating electromagnetic field (light wave) with polarization direction $\hat{\varepsilon}$, the perturbation becomes

$$H'(t) = -\frac{i\hbar e}{m}A_0 e^{i(\overrightarrow{k}\cdot\overrightarrow{r}-\omega t)}\hat{\varepsilon}\cdot\overrightarrow{\nabla} + c.c. \tag{9.99}$$

The time-dependent term with $e^{i\omega t}$ is analogous to the periodic perturbation, which we already calculated in equation (9.86). Now we concentrate on the other part

$$H'_{mi} \propto \int \psi^*_m(\overrightarrow{r})e^{i(\overrightarrow{k}\cdot\overrightarrow{r})}\hat{\varepsilon}\cdot\overrightarrow{\nabla}\psi_i(\overrightarrow{r})dV. \tag{9.100}$$

For the phase factor $e^{i(\overrightarrow{k}\cdot\overrightarrow{r})}$ it is

$$e^{i(\overrightarrow{k}\cdot\overrightarrow{r})} = \sum_{n=0}^{\infty}\frac{(i)^n(\overrightarrow{k}\cdot\overrightarrow{r})^n}{n!}. \tag{9.101}$$

For most of the experiments the atoms are much smaller than the wavelength (except for x-rays) and the phase is constant over the atom ($|\overrightarrow{k}\cdot\overrightarrow{r}| \ll 1$ and $\Rightarrow \lambda \gg a_0$). We can set $i(\overrightarrow{k}\cdot\overrightarrow{r}) = 0$ and the phase term is unity. This is called the dipole approximation ($e^{i(\overrightarrow{k}\cdot\overrightarrow{r})} = 1$), and the next higher approximation the quadrupole approximation ($e^{i(\overrightarrow{k}\cdot\overrightarrow{r})} = i\overrightarrow{k}\cdot\overrightarrow{r}$). With the dipole approximation the integeral becomes

$$\int \psi^*_m(\overrightarrow{r})\hat{\varepsilon}\cdot\overrightarrow{\nabla}\psi_i(\overrightarrow{r})dV = \hat{\varepsilon}\cdot\int \psi^*_m(\overrightarrow{r})\overrightarrow{\nabla}\psi_i(\overrightarrow{r})dV \tag{9.102}$$

The Heisenberg equation of motion reads

$$\overrightarrow{p} = \frac{im}{\hbar}[H_0,\overrightarrow{r}] \Rightarrow \overrightarrow{\nabla} = \frac{i\overrightarrow{p}}{\hbar} = -\frac{m}{\hbar^2}[H_0,\overrightarrow{r}]. \tag{9.103}$$

Inserting (9.103) into (9.102), using $H_0\psi_k = E_0\psi_k$ we have

$$\hat{\varepsilon}\cdot\int\psi_m^*(\overrightarrow{r})\overrightarrow{\nabla}\psi_i(\overrightarrow{r})dV = \hat{\varepsilon}\cdot\left(-\frac{m}{\hbar^2}\right)\int\psi_m^*(\overrightarrow{r})[H_0,\overrightarrow{r}]\psi_i(\overrightarrow{r})dV \quad (9.104)$$

$$= \left(-\frac{m}{\hbar^2}(E_m^{(0)}-E_i^{(0)})\right)\hat{\varepsilon}\cdot\int\psi_m^*(\overrightarrow{r})\overrightarrow{r}\psi_i(\overrightarrow{r})dV$$

$$= \left(-\frac{m\omega_{mi}}{\hbar}\right)\hat{\varepsilon}\cdot\int\psi_m^*(\overrightarrow{r})\overrightarrow{r}\psi_i(\overrightarrow{r})dV \quad (9.105)$$

Here we used $(E_m^{(0)}-E_i^{(0)}) = \omega_{mi}\hbar$.If we insert the vector potential $\overrightarrow{A}$ we have

$$H'_{mi} = -\frac{i\hbar e}{m}A_0\left(-\frac{m\omega_{mi}}{\hbar}\right)\hat{\varepsilon}\cdot\int\psi_m^*(\overrightarrow{r})\overrightarrow{r}\psi_i(\overrightarrow{r})dV \quad (9.106)$$

$$= e\overrightarrow{E}(\omega_{mi})\cdot\int\psi_m^*\overrightarrow{r}\psi_i dV \quad (9.107)$$

$$= -\overrightarrow{E}(\omega_{mi})\cdot\overrightarrow{\underline{\mu}}_{mi} \quad (9.108)$$

where 9.108 describes the interaction of the electromagnetic field with the transition dipole moment. For (for $i = m$) it is the potential energy of an electric dipole in an electric field. The transition dipole moment is given by

$$\overrightarrow{\underline{\mu}}_{mi} = -e\int\psi_m^*\overrightarrow{r}\psi_i dV \quad (9.109)$$

$$= \int\psi_m^*\left(-e\sum_{\ell=1}^{n}\overrightarrow{r_\ell}+e\sum_{k=1}^{N}Z_k\overrightarrow{R_k}\right)\psi_i dV. \quad (9.110)$$

The intensities in dipole approximation are found

$$I(\omega_{mi}) \approx |\hat{\varepsilon}\cdot\int\psi_m^*\left(-e\sum_{\ell=1}^{n}\overrightarrow{r_\ell}+e\sum_{k=1}^{N}Z_k\overrightarrow{R_k}\right)\psi_i dV|^2 = |\hat{\varepsilon}\cdot\overrightarrow{\underline{\mu}}_{mi}|^2 \quad (9.111)$$

where $\hat{\varepsilon}$ is the polarization vector of the electromagnetic field. The selection rules say that transitions are forbidden if $\overrightarrow{\underline{\mu}}_{mi} \equiv 0$. To test if transitions are forbidden symmetry arguments are used and the term $\hat{\varepsilon}\cdot\overrightarrow{r}$ is expressed by spherical harmonics with $\ell = 1$ and $m = 0, \pm 1$:

$$\hat{\varepsilon}\cdot\overrightarrow{r} = \varepsilon_x\sin\vartheta\cos\varphi+\varepsilon_y\sin\vartheta\sin\varphi+\varepsilon_z\cos\vartheta \quad (9.112)$$

$$= \sqrt{\frac{4\pi}{3}}\left\{\left(\frac{\varepsilon_x+i\varepsilon_y}{\sqrt{2}}\right)Y_{1,-1}+\left(\frac{-\varepsilon_x+i\varepsilon_y}{\sqrt{2}}\right)Y_{1,+1}+\varepsilon_z Y_{1,0}\right\} \quad (9.113)$$

Now we investigate the transition from the initial state $\psi_i = \psi_{n_i,\ell_i,m_i}$ to the final state $\psi_f = \psi_{n_f,\ell_f,m_f}$:

$$\langle\hat{\varepsilon}\cdot\overrightarrow{r}\rangle = \int\psi_f^*\hat{\varepsilon}\cdot\overrightarrow{r}\psi_i dV \quad (9.114)$$

$$= \int R_{n_f,\ell_f}^*(r)Y_{\ell_f,m_{\ell_f}}^*(\vartheta,\varphi)\hat{\varepsilon}\cdot\overrightarrow{r}R_{n_i,\ell_i}(r)Y_{\ell_i,m_{\ell_i}}(\vartheta,\varphi)\overrightarrow{r}dV \quad (9.115)$$

Inserting (9.113) we find

$$\int\int Y^*_{\ell_f,m_{\ell_f}}(\vartheta,\varphi)Y_{1,m}(\vartheta,\varphi)Y_{\ell_i,m_{\ell_i}}(\vartheta,\varphi).d\cos\vartheta d\varphi \tag{9.116}$$

$$\int_0^{2\pi} e^{-im_{\ell_f}\varphi}e^{im\varphi}e^{im_{\ell_i}\varphi}d\varphi = \delta_{m+m_{\ell_i}-m_{\ell_f},0} \tag{9.117}$$

The integral (9.117) does not vanish if $m_{\ell_f} - m_{\ell_i} = m = 0, \pm 1$. Thus, our **first selection rule** in dipole approximation is

$$\Delta m_\ell = 0, \pm 1. \tag{9.118}$$

The next selection rule follows from inversion symmetry. The integral $I(\overrightarrow{r})$ should not vanish going from $\overrightarrow{r} \to -\overrightarrow{r}$:

$$I(\overrightarrow{r}) = e\int \psi^*_f \overrightarrow{r}\psi_i d\overrightarrow{r} \propto \int Y^*_{\ell_f,m_{\ell_f}}\overrightarrow{r}Y_{\ell_i,m_{\ell_i}}d\cos\vartheta d\varphi. \tag{9.119}$$

Since $Y_{\ell,m}(\overrightarrow{r}) \to (-1)^\ell Y_{\ell,m}(\overrightarrow{-r})$ the integral is not zero if

$$I(\overrightarrow{-r}) = (-1)^{\ell_f}(-1)(-1)^{\ell_i}I(\overrightarrow{r}) > 0. \tag{9.120}$$

This is only the case if $\ell_f + \ell_i + 1 = 0, \pm 2, \ldots$ and we can directly conclude that

$$\Delta\ell \neq 0. \tag{9.121}$$

To specify the selection rule for the quantum number ℓ further we remember, that we can write the product of two spherical harmonics with ℓ_1 and ℓ_2 as a sum of spherical harmonics with quantum numbers ℓ ranging from $|\ell_2 - \ell_1|$ to $|\ell_2 + \ell_1|$.

$$Y_{1,m}Y_{\ell_i,m_{\ell_i}} = \alpha Y_{\ell_i+1,m_{\ell_i}+m} + \beta Y_{\ell_i,m_{\ell_i}+m} + \gamma Y_{\ell_i-1,m_{\ell_i}+m} \tag{9.122}$$

Inserting this into (9.116) we have

$$\int\int Y^*_{l_f,m_{\ell_f}}(\alpha Y_{\ell_i+1,m_{\ell_i}+m} + \beta Y_{\ell_i,m_{\ell_i}+m} + \gamma Y_{\ell_i-1,m_{\ell_i}+m})d\cos\vartheta d\varphi. \tag{9.123}$$

Using the orthonormality of $\{Y_{\ell,m}\}$ the integral does not vanish for

$$\ell_f = \{\ell_i + 1, \quad \ell_i, \quad \ell_i - 1\} \tag{9.124}$$

$$\Rightarrow \Delta\ell = \pm 1 \tag{9.125}$$

In summary we have selection rules for dipole approximation

$$\Delta m = 0, \pm 1 \tag{9.126}$$

$$\Delta\ell \neq 0 \tag{9.127}$$

$$\Delta\ell = \pm 1. \tag{9.128}$$

If we apply these rules to the normal Zeeman effect we have to analyze the integral

$$\int Y^*_{\ell_f,m_{\ell_f}} \left\{ \left(\frac{\varepsilon_x + i\varepsilon_y}{\sqrt{2}} \right) Y_{1,-1} + \left(\frac{-\varepsilon_x + i\varepsilon_y}{\sqrt{2}} \right) Y_{1,+1} + \varepsilon_z Y_{1,0} \right\} Y_{\ell_i,m_{\ell_i}} d\cos\vartheta d\varphi \tag{9.129}$$

with the magnetic field $\overrightarrow{B}$ is parallel to the z-axis (see experimental setup).

For **longitudinal (L)** observation direction we have $\varepsilon_z = 0$, since the electromagnetic field is a transverse wave.

- $m_{\ell_f} = m_{\ell_i}+1$: Polarization vector is given by $1/\sqrt{2}(\varepsilon_x - i\varepsilon_y)$, which describes (right handed) circular polarized light σ_-.
- $m_{\ell_f} = m_{\ell_i}-1$: Polarization vector is given by $1/\sqrt{2}(\varepsilon_x + i\varepsilon_y)$, which describes (left handed) circular polarized light σ_+.

Note, the definition of left handed and right handed circular polarized light is sometimes used the other way around (σ_+ for right handed circular polarization and vice versa).

Along the z-axis the observed transitions are circular polarized. In this experimental geometry the angular momentum of the photon is parallel to the $\overrightarrow{k}$ direction (in z-direction). We have conservation of angular momentum or spin with the spin of the photon to be $m_s = \pm\hbar$. Thus, the case $m = 0$ is not possible, because upon absorption/emission the angular momentum will change. For

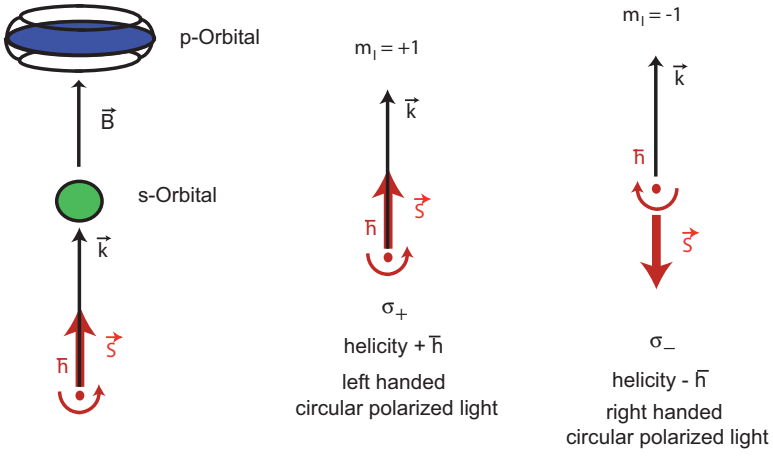


Abbildung 9.3. Interaction of right and left handed circular polarized light with matter. Since we have conservation of angular momentum or spin only such transitions are allowed which result in spin changes of $\Delta\hbar m_{s,ph}$.

photon absorption of $m_s = 1$ we have $\Delta m_\ell = 1$, for photon emission $\Delta m_\ell = -1$.

For photon absorption of $m_s = -1$ we have $\Delta m_\ell = -1$, for photon emission $\Delta m_\ell = +1$.

For **transverse (T)** observation direction we have $\varepsilon_x = 0$, since the electromagnetic field is a transverse wave. Now we have three terms resulting in transitions:

- $m_{\ell_f} = m_{\ell_i}$, here only the term with $\varepsilon_z \neq 0$ is relevant; the light is linearly polarized in z-direction.
- $m_{\ell_f} = m_{\ell_i} \pm 1$ the contributing term is $Y_{1,\pm 1}$ and the light is linearly polarized in y-direction.

Another way to argue is that if one applies light polarized in z-direction ($\varepsilon_y = 0$), only transitions with $\Delta m = 0$ (with $Y_{1,m}$) are possible. Light polarized in y-direction ($\varepsilon_z = 0$) can result in transitions to $\Delta m = \pm 1$ (depending on the frequencies).

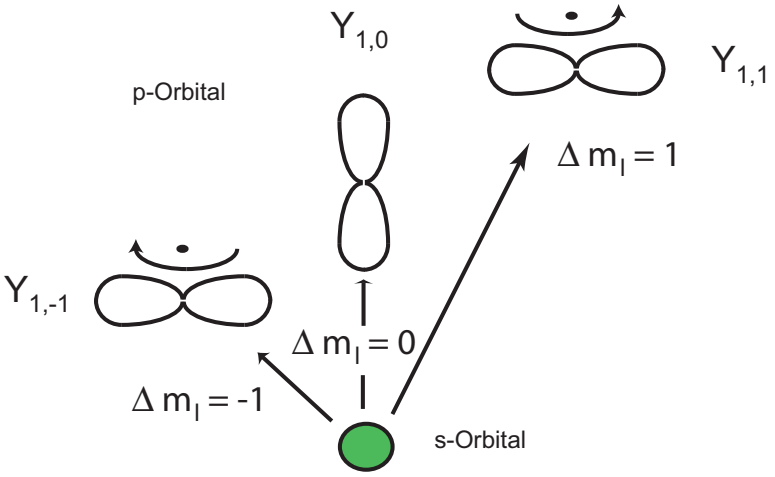


Abbildung 9.4. Interaction of light polarized in ε_y and ε_z direction with a s-orbital.

- The vector $\overrightarrow{\mu}_{mi}$ indicates a charge redistribution going from $|\psi_i|^2$ to $|\psi_f|^2$ described by the transition dipole moment. Upon absorption the atomic 'size' is growing.
- The developing parameter in $e^{i\overrightarrow{k}\cdot\overrightarrow{r}}$ is $\overrightarrow{k}\cdot\overrightarrow{r}$, which is approximately of the size

$$\overrightarrow{k}\cdot\overrightarrow{r} \approx ka_0 = \frac{\omega a_0}{c_0} = \frac{\hbar\omega a_0}{\hbar c}. \tag{9.130}$$

With the transition energy of $\Delta E \approx \frac{\hbar^2}{2ma_0^2}$ in a hydrogen atom we find

$$\begin{aligned} \overrightarrow{k} \cdot \overrightarrow{r} &\approx \frac{\hbar^2}{2ma_0^2}\frac{a_0}{\hbar c_0} && (9.131) \\ &\approx \frac{\hbar}{ma_0 c_0} = \frac{\hbar}{mc_0}\frac{me^2}{4\pi\varepsilon_0\hbar^2} = \frac{e^2}{4\pi\varepsilon_0\hbar c_0} = \alpha \simeq \frac{1}{137} && (9.132) \end{aligned}$$

with α the fine structure constant, which is a fundamental constant for the coupling strengths between charged particles and the electromagnetic field. In the development of $e^{i\overrightarrow{k}\cdot\overrightarrow{r}}$ every next term will result in contributions of order

$$\mathcal{O}(\alpha^2) \approx 10^{-4}. \tag{9.133}$$

- The next term after the dipole approximation contains the electric quadrupole and magnetic dipole contributions, which have different selection rules than the electric dipole transitions, e.g. $\Delta\ell = 2$. But the intensities of those transitions are weaker by a factor of $\approx 10^{-4}$:

$$\int \psi_m^*(\overrightarrow{r}) i(\overrightarrow{k}\cdot\overrightarrow{r})(\hat{\varepsilon}\cdot\overrightarrow{\nabla})\psi_i d\overrightarrow{r} \tag{9.134}$$

inserting $\overrightarrow{p} \propto \overrightarrow{\nabla}$ we find

$$\begin{aligned} (\overrightarrow{k}\cdot\overrightarrow{r})(\hat{\varepsilon}\cdot\overrightarrow{p}) &= \frac{1}{2}\left[(\overrightarrow{k}\cdot\overrightarrow{r})(\hat{\varepsilon}\cdot\overrightarrow{p}) + (\hat{\varepsilon}\cdot\overrightarrow{r})(\overrightarrow{k}\cdot\overrightarrow{p})\right] \\ &\quad + \frac{1}{2}\left[(\overrightarrow{k}\cdot\overrightarrow{r})(\hat{\varepsilon}\cdot\overrightarrow{p}) - (\hat{\varepsilon}\cdot\overrightarrow{r})(\overrightarrow{k}\cdot\overrightarrow{p})\right] && (9.135) \\ &= I + II \\ &= I + \frac{1}{2}(\overrightarrow{k}\times\hat{\varepsilon})\cdot(\overrightarrow{r}\times\overrightarrow{p}). && (9.136) \end{aligned}$$

Since $(\overrightarrow{k}\times\hat{\varepsilon}) \propto \overrightarrow{B}$, and $(\overrightarrow{r}\times\overrightarrow{p}) \propto \overrightarrow{L}$ the second term (II) gives

$$-\overrightarrow{B}\cdot\overrightarrow{\mu}_{fi} = -\overrightarrow{B}\cdot\int\psi_f^*(-\mu_B\frac{\overrightarrow{L}}{\hbar})\psi_i d\overrightarrow{r} = \overrightarrow{B}\cdot\int\psi_f^*(\frac{e}{2m}\overrightarrow{r}\times\overrightarrow{p})\psi_i d\overrightarrow{r}. \tag{9.137}$$

This is the interaction of the magnetic field with the magnetic transition dipole moment $\overrightarrow{\mu}_{fi}$, leading to the splitting of the degenerate levels of m in a hydrogen atom in the Zeeman experiment. The first term (I) can also be transformed using $\overrightarrow{p} = [H_0, \overrightarrow{r}]\frac{im}{\hbar}$, $H_0\psi_k = E_0\psi_k$, and $\overrightarrow{k}\cdot\hat{\varepsilon} = 0$ and we have

$$\begin{aligned} I &\propto \sum_{i,j=1}^{3} k_i\hat{\varepsilon}_j Q_{ij} && (9.138) \\ Q_{ij}^{fm} &\equiv -e\int\psi_f^*(3x_ix_j - r^2\delta_{ij})\psi_m d\overrightarrow{r}. && (9.139) \end{aligned}$$

Q is the electronic quadrupole transition moment for transitions from $m \rightarrow f$ with $k_i \hat{\varepsilon}_j$ being the components of the gradient of $\overrightarrow{E}$ ($x_1 = x$, $x_2 = y$, $x_3 = z$. Both terms I and II result in new selection rules for electronic quadrupole transitions and magnetic dipole transitions.

- The parity operator P is also a very useful operator, that commutes with V, H, $\overrightarrow{L}^2$, and L_z. The quantum number α of the parity operator, here acting on the spherical harmonics is

$$PY_{l,m} = \alpha Y_{l,m} = (-1)^{\ell} Y_{lm}. \tag{9.140}$$

Eigenvalues of the parity operator are $\alpha = \pm 1$.

10 Spin of the electron

We already introduced the Spin of an electron to be $s = \frac{1}{2}$. The Spin operator $\overrightarrow{S}$ operates in a two dimensional spin space an exhibits the properties of an angular momentum operator with quantum numbers $m_s = \pm\frac{1}{2}$. Several experiments result in the hypothesis of the electron spin. The Stern Gerlach experiment is shown in Fig. 10, the anomalous Zeeman effect (with the Na D doublet) and the general doublet structure of spectral lines. The new effects found in those expe-

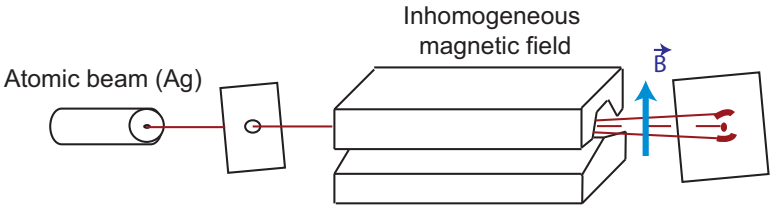


Abbildung 10.1. Stern Gerlach experiment. An atomic beam splits in two parts in an inhomogeneous magnetic field along the z-axis which is parallel to the average magnetic field direction.

riments were explained by an additional interaction to the magnetic moment of the electron spin. In Stern Gerlach experiment silver atoms were sent through an inhomogeneous magnetic field resulting in a splitting of two spots, with a splitting proportional to the field gradient. The explanation for this observation is the interaction of the magnetic field $\overrightarrow{B}$ (here in z-direction) with a magnetic moment $\overrightarrow{\mu}_s$

$$V = -\overrightarrow{\mu}_s \cdot \overrightarrow{B} \tag{10.1}$$

$$\overrightarrow{F} = -\overrightarrow{\nabla} V = \overrightarrow{\nabla}(\overrightarrow{\mu}_s \cdot \overrightarrow{B}) \tag{10.2}$$

$$F_z = \mu_{s_z} \frac{\partial}{\partial z} B_z. \tag{10.3}$$

In a classical picture all possible magnetic dipole directions would be allowed and no distinct spots would be visible in the experiment. Quantum mechanically the magnetic moment $\overrightarrow{\mu}$ is correlated with the orbital angular momentum quantum number ℓ which can take on $2(\ell+1)$ distinct values (odd number). The two spots observed in the Stern Gerlach experiment could not be explained with the orbital angular momentum. Additionally, experiments with hydrogen ($\ell = 0$) show similar results, so that a magnetic moment $\overrightarrow{\mu}_s$ due to the spin of an electron was introduced

$$\begin{aligned}
\overrightarrow{\mu}_s &= -g_s\mu_B\frac{\overrightarrow{S}}{\hbar} && (10.4)\\
g_s &= 2(1+\frac{\alpha}{2\pi}-0.328\frac{\alpha^2}{\pi^2}+\ldots) = 2.002319310(6) \quad \text{Q.E.D} && (10.5)\\
g_s &= 2.002319314(7) \quad \text{Experiment (1971)} && (10.6)\\
\overrightarrow{\mu} &= -g_L\mu_B\frac{\overrightarrow{L}}{\hbar} && (10.7)\\
g_L &= 1. && (10.8)
\end{aligned}$$

The g-factor is the gyromagnetic ratio of the magnetic moment (in μ_B) to the angular momentum (in $\hbar$). The Stern Gerlach experiment shows that $\overrightarrow{\mu}_{s_z} \approx \pm\mu_B$ and thus $g_s \approx 2$. As a result the different angular momenta $\overrightarrow{L}$ and $\overrightarrow{S}$ add to a general angular momentum $\overrightarrow{J}$

$$\overrightarrow{J} = \overrightarrow{L} + \overrightarrow{S}. \tag{10.9}$$

The magnetic moments add up to $\overrightarrow{\mu}_J$

$$\overrightarrow{\mu}_J = \overrightarrow{\mu}_L + \overrightarrow{\mu}_s \approx -\frac{\mu_B}{\hbar}[\overrightarrow{L} + 2.0023\,\overrightarrow{S}]. \tag{10.10}$$

Note, $\overrightarrow{J}$ and $\overrightarrow{\mu}_J$ are not parallel (if there is an effective spin). All atoms with a single outermost electron in the s-orbital show the same splitting in the Stern Gerlach experiment. Therefore, the magnetic moments of the other spins in a closed shell cancel each other out. This is in accordance with $\sum_{m=-\ell}^{\ell} |Y_{\ell m}|^2 = c$.

The spin introduces two additional terms to the SE

$$\begin{aligned}
H'_{mag} &= -\overrightarrow{\mu}_s \cdot \overrightarrow{B}_{ext} && (10.11)\\
H'_{SL} &= -\overrightarrow{\mu}_s \cdot \overrightarrow{B}_{orbit} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\overrightarrow{L}\cdot\overrightarrow{S} = \xi(r)\overrightarrow{L}\cdot\overrightarrow{S} && (10.12)
\end{aligned}$$

The term (10.12) is the potential energy of $\overrightarrow{\mu}_s$ in the internal magnetic field $\overrightarrow{B}_{orbit}$ introduced by the 'moving' electron itself. In the system where the electron is at

the origin with velocity zero, the nucleus is 'moving' and creates a magnetic field of $\overrightarrow{B} \propto \frac{1}{2m^2c^2e}\frac{1}{r}\frac{dV}{dr}\overrightarrow{L}$ with the potential $V = -\frac{Ze^2}{4\pi\varepsilon_0 r}$. This term is called *spin-orbit interaction*, explaining the doublet structure of spectral lines.

Alkali metals have only one valence electron and if $\ell \neq 0$ we have to take into account the $\overrightarrow{L} \cdot \overrightarrow{S}$ term. The electron spin can be oriented parallel or antiparallel to $\overrightarrow{L}$.

Example Na with 11 electrons (one valence electron):
$[(1s)^2|(2s)^2(2p_x)^2(2p_y)^2(2p_z)^2|3s]$
Since the inner shells screen the nucleus charges the effective potential for the valence electron is

$$V_{eff} = -\frac{\alpha(r)}{r}. \tag{10.13}$$

For small distances the potential is the Coulomb potential with nucleus charge Z, and for large distances the effective nucleus charge is $Z = 1$. Assuming a transition from $3p \rightarrow 3s$ the $\overrightarrow{L} \cdot \overrightarrow{S}$ coupling introduces a splitting of the ℓ degenerated states and we find a doublet structure of transitions (see Fig. 10). In sodium atoms we

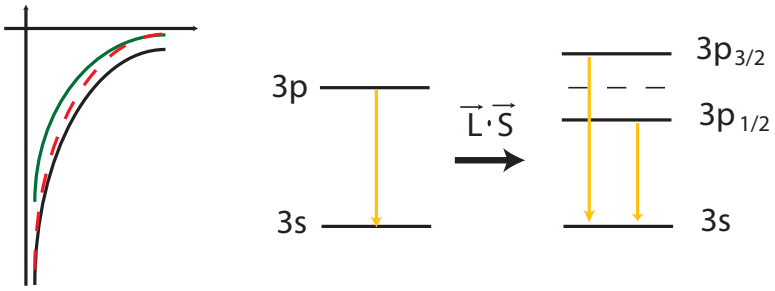


Abbildung 10.2. Screening of the nucleic charge by the inner electrons; green: Coulomb potential with $Z = 1$; black: Coulomb potential with Z; red: effective potential due to screening. Degenerate transitions from the $3p \rightarrow 3s$ orbital will split because the total angular momentum quantum number is $j = \ell \pm s = 1 \pm \frac{1}{2}$ and allows two terms.

find two transitions from $3p \rightarrow 3s$ with D_1, 589.59 nm and D_2, 588.96 nm ($3s$ do

not split). An estimation of the spin-orbit interaction strength for atoms is

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \Rightarrow \frac{dV}{dr} = \frac{e^2}{4\pi\varepsilon_0 r^2} \tag{10.14}$$

$$\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\overrightarrow{L}\cdot\overrightarrow{S} \approx \frac{e^2}{8\pi\varepsilon_0 m^2 c_0^2 r^3}\hbar^2$$

$$\text{with} \quad \langle\frac{1}{r^3}\rangle_{n=2,\ell=1} = \frac{1}{(3a_0)^3} \tag{10.15}$$

$$-\overrightarrow{\mu}_s\cdot\overrightarrow{B}_{orbit} \approx 0.4\,10^{-23}\,\mathrm{J} \approx 0.25\,10^{-4}\,\mathrm{eV} \approx 0.2\,\mathrm{cm}^{-1} \tag{10.16}$$

$$with \quad \mu_s \approx \mu_B \approx 10^{-23}\,\mathrm{Am}^2 \tag{10.17}$$

$$\Rightarrow \overrightarrow{B}_{orbit} \approx \frac{10^{-23}\,\mathrm{J}}{10^{-23}\,\mathrm{Am}^2} \approx 1\,\mathrm{Tesla} \tag{10.18}$$

The internal magnetic field leading to spin-orbit interaction is of the strength of external magnetic fields (Zeeman effect).

10.1 Spin-orbit and additional couplings

The orbital angular momentum operator $\overrightarrow{L}$ acts on the spatial coordinates, while the spin operator $\overrightarrow{S}$ acts only on the spin coordinates. Therefore both operators commute and we can add them to the general angular momentum operator $\overrightarrow{J}$

$$\left[\overrightarrow{L},\overrightarrow{S}\right] = 0 \tag{10.19}$$

$$\overrightarrow{J} = \overrightarrow{L}+\overrightarrow{S} \tag{10.20}$$

$$[J_i, J_j] = i\hbar J_k, \quad (\mathrm{i}=\mathrm{x,y,z};\ \mathrm{j}=\mathrm{y,z,x};\ \mathrm{k}=\mathrm{z,x,y}). \tag{10.21}$$

There exist simultaneous eigenfunctions ψ_{jm_j} of $\overrightarrow{J}^2$ and J_z

$$\overrightarrow{J}^2\psi_{jm_j} = j(j+1)\hbar^2\psi_{jm_j} \quad \mathrm{j}=\{0,\,\frac{1}{2},\,1,\,\frac{3}{2},\,\ldots\} \tag{10.22}$$

$$J_z\psi_{jm_j} = m_j\hbar\psi_{jm_j} \quad \mathrm{m_j}=\{-\mathrm{j},\,-\mathrm{j}+1,\,\ldots,\,\mathrm{j}\}. \tag{10.23}$$

Without coupling $\overrightarrow{L}\cdot\overrightarrow{S}=0$ the wave functions are

$$\psi_{n\ell m_\ell s m_s} \propto R_{n\ell}(r)Y_{\ell m}(\vartheta,\varphi)\chi_{sm_s} \tag{10.24}$$

$$\chi_{1/2,1/2} = \begin{pmatrix}1\\0\end{pmatrix}; \quad \chi_{1/2,-1/2} = \begin{pmatrix}0\\1\end{pmatrix}. \tag{10.25}$$

With $\overrightarrow{L}\cdot\overrightarrow{S}\neq 0$ the quantum numbers m_ℓ and m_s are no good quantum numbers any more, since $[H_0, L_z]\neq 0$ and $[H_0, S_z]\neq 0$. We need a new basis of simultaneous eigenfunctions of the operators $\overrightarrow{L}^2$, $\overrightarrow{S}^2$, $\overrightarrow{J}^2$, J_z, which commute with each

other and with $\overrightarrow{L} \cdot \overrightarrow{S}$, and H_0. The new eigenfunctions are of the type $\psi_{njm_j\ell s}$ and for a given ℓ the possible values for j are (vector model)

$$|\ell - s| \leq j \leq |\ell + s|. \tag{10.26}$$

If we take H'_{SL} as a perturbation

$$\begin{aligned} H'_{SL} &= \xi(r)\overrightarrow{L} \cdot \overrightarrow{S} && (10.27)\\ &= \xi(r)\frac{1}{2}(\overrightarrow{J}^2 - \overrightarrow{L}^2 - \overrightarrow{S}^2) && (10.28) \end{aligned}$$

with $\psi_{njm_j\ell s}$ as the eigenfunctions of the unperturbed system with eigenvalues of E_n, $j(j+1)\hbar^2$, $m_j\hbar$, $\ell(\ell+1)\hbar^2$, $s(s+1)\hbar^2$ then we can calculate the energy shifts in first order perturbation theory for the hydrogen atom.

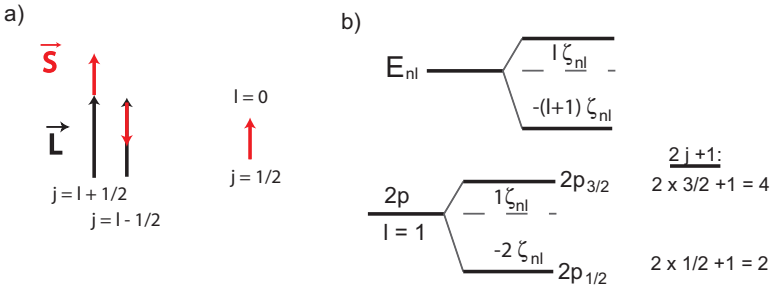


Abbildung 10.3. Spin-orbit coupling in a hydrogen atom. a) possible relative orientations of vectors L and S to each other; b) level splitting due to spin-orbit interaction and the number of degeneracy (2j+1) for each level.

$$\begin{aligned} \Delta E_{SL} &= \int \psi^*_{njm_j\ell s}\left\{\xi(r)\frac{1}{2}(\overrightarrow{J}^2 - \overrightarrow{L}^2 - \overrightarrow{S}^2)\right\}\psi_{njm_j\ell s}d\overrightarrow{r} && (10.29)\\ &= \frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - \frac{3}{4}\right]\langle\xi(r)\rangle. && (10.30) \end{aligned}$$

For a hydrogen atom $\langle \xi(r) \rangle$ can be calculated exactly

$$\left\langle \frac{1}{r^3} \right\rangle_{n\ell m} = \frac{Z^3}{a_0^3 n^3 \ell(\ell+\frac{1}{2})(\ell+1)} \tag{10.31}$$

$$\langle \xi(r) \rangle = \frac{1}{2m^2c_0^2} \frac{Ze^2}{4\pi\varepsilon_0} \frac{Z^3}{a_0^3 n^3 \ell(\ell+\frac{1}{2})(\ell+1)} \tag{10.32}$$

$$\overset{\ell=0\ j=1/2}{\Rightarrow} \quad \Delta E_{SL} = 0 \tag{10.33}$$

$$\overset{\ell\neq 0\ j=\ell+1/2}{\Rightarrow} \quad j(j+1) - \ell(\ell+1) - \frac{3}{4} = \ell \tag{10.34}$$

$$\overset{\ell\neq 0\ j=\ell-1/2}{\Rightarrow} \quad j(j+1) - \ell(\ell+1) - \frac{3}{4} = -\ell - 1 \tag{10.35}$$

$$\left(\frac{1}{a_0}\right)^3 = \left(\frac{\alpha mc}{\hbar}\right)^3, \quad \text{with} \quad \alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c_0} \tag{10.36}$$

$$\Delta E_{SL} = \underbrace{\left(\frac{mc^2(Z\alpha)^4}{4n^3\ell(\ell+\frac{1}{2})(\ell+1)}\right)}_{\zeta_{n\ell}} \cdot \begin{cases} \ell, & j = \ell + \frac{1}{2} \\ -\ell - 1, & j = \ell - \frac{1}{2} \end{cases} \tag{10.37}$$

$$\Delta E_{SL,\ell+1/2} = \ell\, \zeta_{n\ell}, \qquad j = \ell + \frac{1}{2} \tag{10.38}$$

$$\Delta E_{SL,\ell-1/2} = -(\ell+1)\, \zeta_{n\ell}, \qquad j = \ell - \frac{1}{2} \tag{10.39}$$

The energy splitting is proportional to the 4th power of the nuclear charge and 4th power of the fine structure constant $\Delta E_{SL} \propto (Z\alpha)^4$. The term $\zeta_{n\ell}$ is always positive so that we have a splitting in two levels, one is energetically higher ($j = \ell + \frac{1}{2}$) and the other one is energetically lower ($j = \ell - \frac{1}{2}$). Thus, the degeneracy due to ℓ is reduced, but there is still some degeneracy left ($2j+1$). The splitting in two levels was thought to explain the doublet line structure, but the calculations do not fit with the experimental results! This is because of the fact that the SE does not contain any relativistic corrections. The relativistic expression for the kinetic energy of an electron is $E_{kin} = \sqrt{p^2c_0^2 + m^2c_0^4} - mc_0^2$, which can be developed in a Taylor expansion. Relativistic corrections are included in the Dirac

equation (next order correction terms)

$$
\begin{aligned}
E'\psi &= \left[-\frac{\hbar^2}{2m}\overrightarrow{\nabla}^2 + V(r) + \frac{\hbar^2(E'-V(r))}{4m^2c_0^2}\overrightarrow{\nabla}^2\right. \\
&\quad \left. + \frac{1}{2m^2c_0^2 r}\frac{dV}{dr}\overrightarrow{L}\cdot\overrightarrow{S} - \frac{\hbar^2}{4m^2c_0^2}\frac{dV}{dr}\frac{\partial}{\partial r}\right]\psi \qquad (10.40)\\
H &= \frac{\overrightarrow{p}^2}{2m} + V(r) - \underbrace{\frac{\overrightarrow{p}^4}{8m^3c_0^2}}_{I} + \\
&\quad \underbrace{\frac{1}{2m^2c_0^2 r}\frac{dV}{dr}\overrightarrow{L}\cdot\overrightarrow{S}}_{II} + \underbrace{\frac{\pi\hbar^2 Ze^2}{2m^2c_0^2 4\pi\varepsilon_0}\delta(\overrightarrow{r})}_{III} \qquad (10.41)\\
E &= E_{n\ell} + \Delta E_{LS} + \Delta E_{rel.} + \Delta E_{Dar} \qquad (10.42)\\
\Delta E_{rel.} &= -\frac{mc_0^2(Z\alpha)^4}{2}\left[\frac{1}{n^3(\ell+\frac{1}{2})} - \frac{3}{4n^4}\right] \qquad (10.43)\\
\Delta E_{Dar} &= \begin{cases} \frac{mc_0^2}{2}\frac{(Z\alpha)^4}{n^3}, & \ell = 0 \\ 0, & else \end{cases} \qquad (10.44)\\
E_{nj} &= E_n\left[1 + \frac{(Z\alpha)^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right] \qquad (10.45)\\
E_{nj}^{exact} &= mc^2\left\{\sqrt{1+\left(\frac{Z\alpha}{n-j-1/2+\sqrt{(j+1/2)^2-Z^2\alpha^2}}\right)^2} - 1\right\}.
\end{aligned}
$$

The term I is the second term of the Taylor expansion and the next term for relativistic corrections to the kinetic energy and does not act on the spin variable. Term II is the spin-orbit coupling, introducing an explicit coupling between $\overrightarrow{L}$ and $\overrightarrow{S}$. Term III is called Darwin term and is only relevant for $\ell = 0$ where $\delta(\overrightarrow{r})$ is not vanishing. This term does not act on the spin variable.

The exact solution E_{nj}^{exact} is obtained by solving the Dirac equation for the Coulomb potential. E_{nj} agrees with the exact solution up to order $(Z\alpha)^2$. The energy levels depend only on the principal quantum number n and the total angular momentum quantum number j, with $j = 1/2,\ 3/2,\ \ldots,\ n-1/2$. To each value of j correspond two possible values of ℓ given by $\ell = j \pm 1/2$, except for $j = n-1/2$ where we find only one state. For example the levels $2p$, $2s$ are split by the spin-orbit coupling and relativistic corrections in 2 levels (doublets) as shown in Fig. 10.1. However, experiments show that there is a (very small) additional splitting of degenerate levels called Lamb shift. In Q.E.D. 'radiative corrections' to the Dirac theory are obtained by taken into account the interaction of the electron with the quantised electromagnetic field. A qualitative explanation given by T.A.

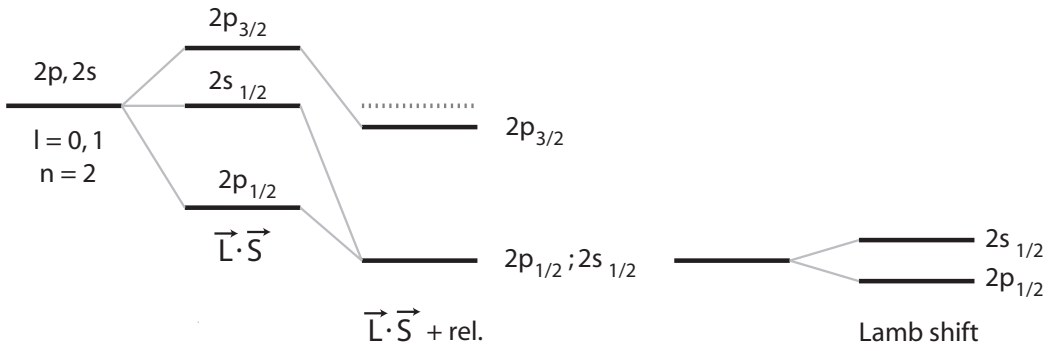


Abbildung 10.4. Spin-orbit coupling in an atom with electron spin 1/2. The spin - orbit coupling alone would split the 2s and the 2p levels into three different levels, but since the total corrections (including relativistic effects) depend only on n and j we end up with two levels of different total angular momentum quantum number j. Additional splitting of the levels is introduced due to the Lamb shift.

Welton (1948) is that a quantised radiation field in its lowest energy state is not zero, but there exist zero-point oscillations. This means that even in the vacuum there are fluctuations in this zero-point radiation field which can act on the electron, causing it to execute rapid oscillatory motions so that the charge is 'smeared out'. If the electron is bound by a non-uniform electric fiel, as in atomic systems, it will therefore experience a potential which is slightly different from that corresponding to its mean position. In particular, the electron in a one-electron atom is not so strongly attached to the nucleus at short distances. As a result, s states (which are most sensitive to short-distance modifications because $|\psi(0)|^2 \neq 0$ for these states) are raised in energy with respect to other states, for which the corresponding modifications are much smaller. The Lamb shift decreases with increasing ℓ. The modifications of the $s_{1/2}$ level is roughly 10% of the energy difference of $p_{3/2} - p_{1/2}$, so that the $s_{1/2}$ level lies higher than the $p_{1/2}$ level. The $p_{3/2}$ energy levels are shifted about 0.2% of the energy difference $d_{5/2} - d_{3/2}$ of the $d_{5/2}$ and $d_{3/2}$ levels, resulting in an upshift of the $p_{3/2}$ level with respect to the $d_{3/2}$ level. The resulting Lamb shifts are of the order of 0.03 cm^{-1}.

Since the dipole operator $\overrightarrow{D} = -e\overrightarrow{r}$ does not depend on the spin, the selection rules derived above for the quantum number ℓ (in the dipole approximation) remains

$$\Delta\ell = \pm 1 \tag{10.46}$$
$$\Delta j = 0, \pm 1 \tag{10.47}$$

For example we see from Fig. 10.1 that the multiplet $np - n's$ has two components. Thus each line of the Lyman series (hydrogen atom, lower state $n = 1$) is split by the fine structure into a pair of lines called a doublet, corresponding to the

transitions

$$np_{1/2} - 1s_{1/2}, \qquad np_{3/2} - 1s_{1/2}. \tag{10.48}$$

We see that in the case of the Balmer series (lower state $n = 2$) the mulitplet

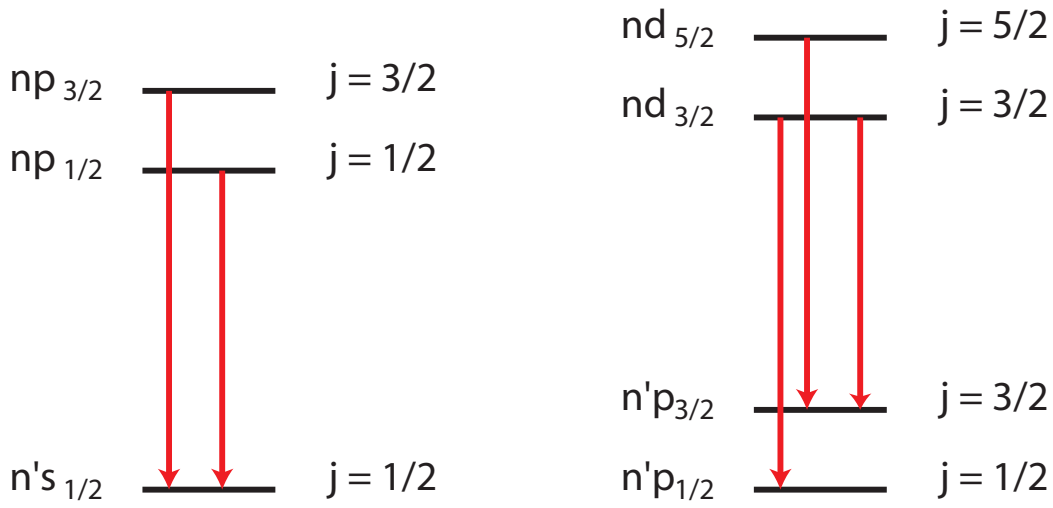


Abbildung 10.5. Transitions of the Lyman series of hydrogen.

$nd - n'p$ has three components and we find seven transitions in total. However, since the levels $ns_{1/2}$ and $np_{1/2}$ coincide, as well as the levels $np_{3/2}$ and $nd_{3/2}$, the Balmer line (see Fig. 10.1) contains five distinct components (without Lamb shift). Since the radial integrals are the same for both transitions $np_{3/2} - n's_{1/2}$ and $np_{1/2} - n's_{1/2}$, it is easy to obtain from the angular parts of those integrals, (that is from angular momentum considerations) the ratio of the two transition probabilities, which is found to be equal to 2. More generally, the ratios of the transition probabilities for the most important special cases are

$$\text{sp trans.} \quad : \quad \frac{s_{1/2} - p_{3/2}}{s_{1/2} - p_{1/2}} = 2 : 1 \tag{10.49}$$

$$\text{pd trans.} \quad : \quad p_{3/2} - d_{5/2} : p_{3/2} - d_{3/2} : p_{1/2} - d_{3/2} = 9 : 1 : 5 \tag{10.50}$$

$$\text{df trans.} \quad : \quad d_{5/2} - f_{7/2} : d_{5/2} - f_{5/2} : d_{3/2} - f_{5/2} = 20 : 1 : 14. \tag{10.51}$$

Under most circumstances the initial states are excited in proportion to their statistical weights, that is the $(2j + 1)$ degenerate levels corresponding to an initial state are equally populated. In this case the ratios of line intensities are the same as those of the corresponding transition probabilities (for different values of m_j).

In the case of the **anomalous Zeeman effect** the internal field or the spin-orbit

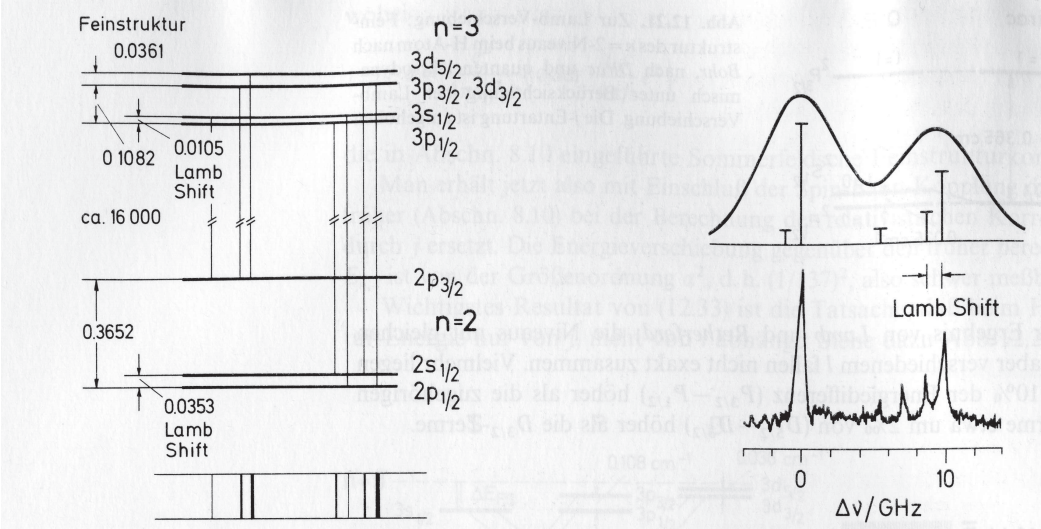


Abbildung 10.6. Structure of the H_α lines of hydrogen and term scheme. The expected optical spectrum is shown at the bottom of the picture, thicker lines correspond to stronger transitions. Energies are given in wavenumbers.

coupling is dominant and the external magnetic field is weak and is treated as the perturbation. The unperturbed Hamiltonian is

$$H_0 = -\frac{\hbar^2}{2m}\triangle - \frac{Ze^2}{4\pi\varepsilon_0 r} + \xi(r)\,\overrightarrow{L}\cdot\overrightarrow{S} \tag{10.52}$$

with $\psi_{njm_j\ell s}$ eigenfunctions of the unperturbed system and eigenfunctions of $\{\overrightarrow{J}^2,\ \overrightarrow{L}^2,\ \overrightarrow{S}^2,\ J_z\}$. The perturbation is

$$\begin{aligned} H' &= -\overrightarrow{\mu}_J\cdot\overrightarrow{B} = -\overrightarrow{\mu}_L\cdot\overrightarrow{B} - \overrightarrow{\mu}_S\cdot\overrightarrow{B} && (10.53)\\ &= \frac{\mu_B}{\hbar}B_z(L_z+2S_z) = \frac{\mu_B}{\hbar}B_z(J_z+S_z) && (10.54)\end{aligned}$$

To first order perturbation theory the energy shift is

$$\Delta E = \frac{\mu B_z}{\hbar}\int \psi^*_{njm_j\ell s}(J_z+S_z)\psi_{njm_j\ell s}d\overrightarrow{r} \tag{10.55}$$

The first term is easy to evaluate $(m_j\hbar)$ but the second term is problematic and is a result of $g_S = 2$.

$$\Delta E = \mu B_z m_j + \frac{\mu B_z}{\hbar}\int \psi^*_{njm_j\ell s}(S_z)\psi_{njm_j\ell s}d\overrightarrow{r} \tag{10.56}$$

To analyze the second term we use the following operator identity and examine its expectation value in the Dirac notation

$$
\begin{aligned}
2i\hbar\overrightarrow{V} &= \overrightarrow{J}\times\overrightarrow{V}+\overrightarrow{V}\times\overrightarrow{J} && (10.57)\\
\left[\overrightarrow{J}^2,[\overrightarrow{J}^2,\overrightarrow{V}]\right] &= 2\hbar^2(\overrightarrow{J}^2\overrightarrow{V}+\overrightarrow{V}\overrightarrow{J}^2)-4\hbar^2(\overrightarrow{V}\cdot\overrightarrow{J})\overrightarrow{J} && (10.58)\\
\langle\ell sjm_j|\overrightarrow{V}\overrightarrow{J}^2|\ell sjm_j\rangle &= 2\langle\ell sjm_j|(\overrightarrow{V}\cdot\overrightarrow{J})\overrightarrow{J}|\ell sjm_j\rangle && (10.59)\\
j(j+1)\hbar^2\langle\ell sjm_j|\overrightarrow{S}_z|\ell sjm_j\rangle &= 2\langle\ell sjm_j|(\overrightarrow{S}\cdot\overrightarrow{J})\overrightarrow{J}_z|\ell sjm_j\rangle && (10.60)\\
j(j+1)\hbar^2\langle\ell sjm_j|\overrightarrow{S}_z|\ell sjm_j\rangle &= 2\hbar m_j\langle\ell sjm_j|\frac{\overrightarrow{J}^2-\overrightarrow{L}^2+\overrightarrow{S}^2}{2}|\ell sjm_j\rangle && (10.61)\\
j(j+1)\hbar^2\langle S_z\rangle &= \hbar m_j\langle jm_j\ell s|\frac{\hbar^2}{2}[j(j+1)-\ell(\ell+1)+s(s+1)]|jm_j\ell s\rangle && (10.62)
\end{aligned}
$$

and we can conclude

$$\langle jm_j\ell s|S_z|jm_j\ell s\rangle=\hbar m_j\frac{j(j+1)-\ell(\ell+1)+s(s+1)}{2j(j+1)}. \tag{10.63}$$

Inserting (10.63) we find the energy shift

$$
\begin{aligned}
\Delta E_{mj} &= \mu_B B_z m_j+\frac{\mu_B B_z}{\hbar}\langle jm_j\ell s|S_z|jm_j\ell s\rangle && (10.64)\\
&= \mu_B B_z m_j\underbrace{\left\{1+\frac{j(j+1)-\ell(\ell+1)+s(s+1)}{2j(j+1)}\right\}}_{g_J} && (10.65)\\
&= g_J\mu_B B_z m_j && (10.66)
\end{aligned}
$$

and the term g_J in (10.66) is called Landé factor. We found the interaction term for perturbation theory which is

$$
\begin{aligned}
V_B &= -\overrightarrow{\mu}_{J,eff}\cdot\overrightarrow{B} && (10.67)\\
\overrightarrow{\mu}_{J,eff} &= -g_J\mu_B\frac{\overrightarrow{J}}{\hbar} && (10.68)\\
V_B &= g_J\frac{\mu_B}{\hbar}\overrightarrow{J}\cdot\overrightarrow{B} && (10.69)\\
&= g_J\mu_B B_z m_j && (10.70)
\end{aligned}
$$

The vector $\overrightarrow{\mu}_J$ is not parallel to $\overrightarrow{J}$, but $\overrightarrow{\mu}_{J,eff}$ is parallel to $\overrightarrow{J}$. In the case of $s=0$ the Landé factor becomes $g_J=1=g_L$, and if $\ell=0$ then it is $g_J=2=g_S$. In general this is not the case and we have $g_J\neq 1,\,2$. For a single electron we have $j=l\pm 1/2$ and the energy shifts are

$$\Delta E_{m_j}=\begin{cases}\frac{2\ell+2}{2\ell+1}\mu_B B_z m_j, & j=\ell+\frac{1}{2}\\ \\ \frac{2\ell}{2\ell+1}\mu_B B_z m_j, & j=\ell-\frac{1}{2}\end{cases} \tag{10.71}$$

In contrast to the normal Zeeman effect ($s = 0$) the splitting of the levels are not equidistant any more, because the g-factor is different for different levels. This result in more different transitions.

- $\ell = 0$ (s-state), $g_J = 2 = g_S$
- $\ell = 1$ (p-state), $g_J = \begin{cases} \frac{4}{3}, & j = \frac{3}{2} \\ \frac{2}{3}, & j = \frac{1}{2} \end{cases}$

The selection rules are (dipole approximation)

$$\Delta m_\ell = 0, \pm 1 \quad \Rightarrow \quad \Delta m_j = 0, \pm 1 \tag{10.72}$$

The scheme in Fig. (10.1) explains the observed additional splitting of the sodium D_1 and D_2 lines upon transitions from $3p_{1/2} \rightarrow 3s_{1/2}$ and $3p_{3/2} \rightarrow 3s_{1/2}$, respectively.

The connection between $\overrightarrow{J}$, $\overrightarrow{\mu}_J$ and $\overrightarrow{\mu}_{J,eff}$ can be explained as follows: The vectors $\overrightarrow{L}$ and $\overrightarrow{L}$ are coupled via H_{SL} to $\overrightarrow{J}$ and precesses about the vector $\overrightarrow{J}$ with high velocity $\omega = E_{SL}/\hbar$. The magnetic moment $\overrightarrow{\mu}_J$ also precesses fast about the $\overrightarrow{J}$ direction. $\overrightarrow{J}$ itself precesses slowly about the magnetic field $\overrightarrow{B}$ (z-axis), since the external field is much weaker than the internal field leading to spin-orbit coupling. Averaged over the slow precession only the component of $\overrightarrow{\mu}_J$ that is parallel to $\overrightarrow{J}$ is not averaged out, because during the slow precession about $\overrightarrow{B}$ we average over many round trips of $\overrightarrow{\mu}_J$ about $\overrightarrow{J}$. Taking this model we can calculate $\overrightarrow{\mu}_{J,eff}$ as the projection of $\overrightarrow{\mu}_J$ on $\overrightarrow{J}$.

$$|\overrightarrow{\mu}_{J,eff}| = \overrightarrow{\mu}_J \cdot \frac{\overrightarrow{J}}{J} \tag{10.73}$$

$$E_B = -\overrightarrow{\mu}_{J,eff} \cdot \overrightarrow{B} = -|\overrightarrow{\mu}_{J,eff}| \frac{\overrightarrow{J} \cdot \overrightarrow{B}}{J} \tag{10.74}$$

$$= -\left(\overrightarrow{\mu}_J \cdot \frac{\overrightarrow{J}}{J}\right)\left(\frac{\overrightarrow{J} \cdot \overrightarrow{B}}{J}\right) \tag{10.75}$$

$$= -\frac{\mu_B}{\hbar}\left((\overrightarrow{J} + \overrightarrow{S}) \cdot \frac{\overrightarrow{J}}{J}\right)\left(\frac{\overrightarrow{J} \cdot \overrightarrow{B}}{J}\right) \tag{10.76}$$

$$= \frac{\mu_B B_z}{\hbar} J_z \frac{(\overrightarrow{J}^2 + \overrightarrow{S}) \cdot \overrightarrow{J}}{|\overrightarrow{J}^2|} \tag{10.77}$$

$$= \frac{\mu_B B_z}{\hbar} J_z \left\{ \frac{\overrightarrow{J}^2 + \frac{1}{2}(\overrightarrow{J}^2 + \overrightarrow{S}^2 - \overrightarrow{L}^2)}{\overrightarrow{J}^2} \right\} \tag{10.78}$$

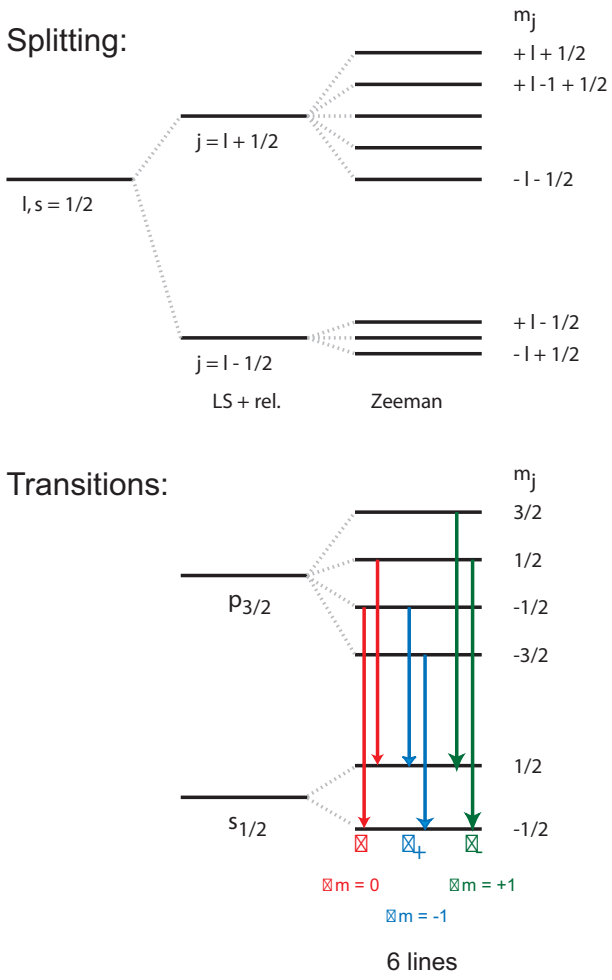


Abbildung 10.7. Splitting of energy levels and transitions induced by the anomalous Zeeman effect. The different energy levels split by different Landé factors. For example the $p_{3/2}$ level split in 4 new levels displaced by $4/3\mu_B B_z$. The $s_{1/2}$ level split in two levels displaced by $2\mu_B B_z$. As a result the 6 transitions have different energies and we observe 6 transitions in total.

If we insert the eigenvalues of $\overrightarrow{J}^2 = \hbar^2 j(j+1)$ and of $\overrightarrow{S}^2$, $\overrightarrow{L}^2$ and J_z we find

$$\begin{aligned}
\langle E_B \rangle &= \Delta E_{m_j} = \frac{\mu_B B_z}{\hbar} \hbar m_j \frac{\hbar^2}{\hbar^2} \left\{ \frac{j(j+1) + \frac{1}{2}[j(j+1) + s(s+1) - \ell(\ell+1)]}{j(j+1)} \right\} \\
&= \mu_B B_z m_j \left[1 + \frac{j(j+1) + s(s+1) - \ell(\ell+1)}{2j(j+1)} \right] \qquad (10.79) \\
&= g_J \mu_B B_z m_j \qquad (10.80)
\end{aligned}$$

10.2 Spin of a nucleus

In addition to the magnetic moment of the spin of the electron, the protons and neutrons of the nucleus have also a total angular momentum $\overrightarrow{I}$, called nuclear spin. The nuclear spin of a proton or neutron is $I = \frac{1}{2}$ and I is the nuclear spin quantum number. The eigenvalues of the operator $\overrightarrow{I}^2$ are $I(I+1)\hbar^2$. The eigenvalues of the operator I_z have possible values of $M_I\hbar$, with $M_I = -I, -I+1, \ldots, I$. A nucleus may possess 2^k-pole moments, with k odd for magnetic moments and k even for electric moments. Here we consider the nucleus as a point dipole with a magnetic dipole moment $\overrightarrow{\mu_I}$ proportional to the nuclear spin $\overrightarrow{I}$.

$$\overrightarrow{\mu}_I = g_I \mu_K \frac{\overrightarrow{I}}{\hbar} \tag{10.81}$$

$$\mu_K = \frac{e\hbar}{2M_p} = \frac{m_e}{M_p}\mu_B = \frac{1}{1836.15}\mu_B \tag{10.82}$$

$$\mu_K = 5.05078 \times 10^{-27}\mathrm{JT}^{-1} \tag{10.83}$$

$$(\overrightarrow{\mu}_I)_z = g_I \mu_K m_I \tag{10.84}$$

Values of the spin, Landé factor and magnetic moment of the nucleons and some nuclei are

Nucleus	Spin I	Landé factor g_I	μ_I (in μ_B)	Natural abundance (%)
proton p	1/2	5.588	2.792	99.88
neutron n	1/2	-3.826	-1.913	-
deuteron ${}^2_1D$	1	0.857	0.857	-
${}^3_2He$	1/2	-4.255	-2.127	-
${}^4_2He$	0	-	0	-
${}^{12}_6C$	0	-	0	-
${}^{13}_6C$	1/2	1.404	0.702	1.1
${}^{16}_8O$	0	-	0	-
${}^{19}_9F$	1/2	5.257	2.628	100
${}^{31}_{15}P$	1/2	2.263	1.131	100
${}^{199}_{80}Hg$	1/2	1.005	0.502	-
${}^{201}_{80}Hg$	3/2	-0.371	-0.556	-

The contributions of the angular momenta were added to a total angular momentum $\overrightarrow{F}$

$$\overrightarrow{F} = \overrightarrow{J} + \overrightarrow{I} \tag{10.85}$$

$$|\overrightarrow{F}| = \hbar\sqrt{F(F+1)}. \tag{10.86}$$

The quantum number F can take on values $F = j + I,\ j + I - 1,\ \ldots,\ j - I$. In total $2I + 1$ or $2j + 1$ possibilities, depending whether I is bigger than j or vice versa. Knowing one of the numbers (I or j) one can determine the other one by counting the number levels in the hyperfine structure. The additional magnetic interaction energy from the hyperfine coupling is

$$\begin{aligned}
\Delta E_{HFS} &= -\overrightarrow{\mu}_I \cdot \overrightarrow{B}_J && (10.87)\\
&= -\mu_I B_J \cos(\angle\, \overrightarrow{\mu}_I,\ \overrightarrow{B}_J) && (10.88)\\
&= g_I \mu_K B_J \frac{F(F+1) - I(I+1) - J(J+1)}{2\sqrt{J(J+1)}} && (10.89)\\
&= \frac{a}{2}[F(F+1) - I(I+1) - J(J+1)] && (10.90)\\
a &= \frac{g_I \mu_K B_J}{\sqrt{J(J+1)}} && (10.91)\\
&= 2\mu_0 \mu_B g_I \mu_K \frac{1}{j(j+1)} |\psi_{n00}(0)|^2 && (10.92)\\
|\psi_{n00}(0)|^2 &= \frac{Z^3}{\pi n^3 a_0^3} && (10.93)\\
\Delta E_{F+1} - \Delta E_F &= a(F+1). && (10.94)
\end{aligned}$$

The magnetic field B_J is the magnetic field induced by the internal electrons at the nucleus. For some atoms the magnetic field is (in Tesla)

	n	$^2S_{1/2}$	$^2P_{1/2}$	$^2P_{3/2}$
Na	3	45	4.2	2.5
K	4	63	7.9	4.6
Rb	5	130	16	8.6
Cs	6	210	28	13

- The constant a is called hyperfine separation constant and can be calculated for $j = 1/2$ by equation (10.92). For s-orbitals the probability density at the nucleus does not vanish and the magnetic field induced by the s-electrons at the nucleus interact with the nucleic magnetic moment. This interaction is called Fermi contact interaction and is isotropic. In the case of $\ell > 0$ the probability density vanishes at the nucleus and the interacting magnetic field B_J results from dipole-dipole interaction between magnetic moment of the electrons and magnetic moment of the nucleus. The hyperfine separation constant becomes anisotropic.

- B_J and ΔE_{HFS} are bigger the smaller the distant of the electrons form the nucleus is. They increase with increasing Z, and decreasing n and ℓ.

- The hyperfine splitting is zero for $I = 0$ or $J = 0$
- For a hydrogen atom the hyperfine separation constant is $a = 1420\,\mathrm{MHz} = 0.0475\,\mathrm{cm}^{-1} = 5.9 \cdot 10^{-6}\mathrm{eV}$
- The hyperfine splitting of spectral lines is small. For $^2S_{1/2}$ of Li the splitting is 0.027 cm^{-1}.
- Without external magnetic field the degeneracy is $(2F + 1)$, with magnetic quantum number m_F.
- The selection rules for optical transitions are $\Delta F = 0, \pm 1$.

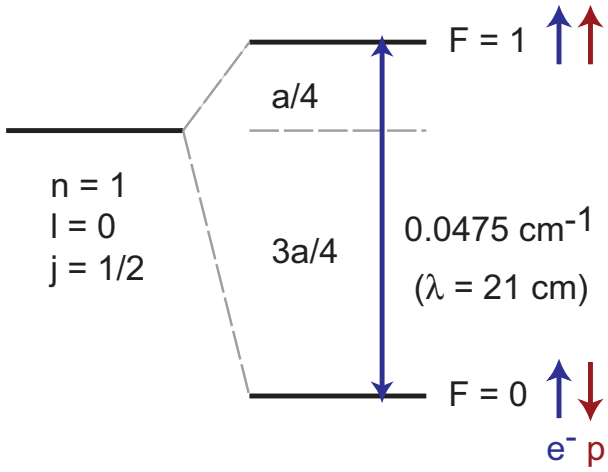


Abbildung 10.8. Hyperfine separation of a hydrogen atom in the ground state. The spin of electron and proton can be oriented parallel (F=1) or antiparallel (F=0). The splitting due to hyperfine interaction (1.420 GHz) is about six times smaller than the Lamb shift.

The energy difference can be measured either directly upon absorption of the matching high frequency radiation leading to a spin flip or by determining the splitting of the spectral lines. By measuring of the energy difference one can calculate the g_S value of the electron to be 2.0023 (magnetic moment of proton and electron is known).

10.2.1 Hyperfine splitting in an external magnetic field

An important tool to investigate the hyperfine structure is applying an external magnetic field $\vec{B}_0$ in addition to the internal field. The resulting splitting of states depend on the relative strengths of both fields. The case of weak external fields $\vec{B}_0$ in comparison to $\vec{B}_J$ is called Zeeman-effect of the hyperfine structure. Here, the coupling of $\vec{I}$, $\vec{J}$, and $\vec{F}$ is maintained and the vectors of $\vec{I}$ and $\vec{J}$ precesses about the $\vec{F}$ vector around the $\vec{B}_0$ direction. The frequency of $\vec{I}$ and $\vec{J}$ about

$\overrightarrow{F}$ is fast in comparison to the precession frequency of $\overrightarrow{F}$ about $\overrightarrow{B}_0$. Therefore, the remaining components are the $F_z = m_F\hbar$ components ($\overrightarrow{B}_0$ parallel to the z-axis) with $m_F = F, F-1, \ldots, -F$. The selection rules are $\Delta F = 0, \pm 1$ and $\Delta m_F = 0, \pm 1$. The energy splitting of the Zeeman hyperfine splitting is

$$\Delta E_{ZHFS} = -\overrightarrow{\mu}_F \cdot \overrightarrow{B}_0 \tag{10.95}$$

$$\Delta E_{ZHFS} = g_F \mu_B B_0 m_F \tag{10.96}$$

$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} - g_I \frac{\mu_K}{\mu_B} \frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)} \tag{10.97}$$

Since $\mu_B \gg \mu_K$ the second term is negligible.

If the external magnetic field becomes stronger, the vectors $\overrightarrow{I}$ and $\overrightarrow{J}$ do not couple any more. The $\overrightarrow{L} \cdot \overrightarrow{S}$ coupling is stronger (coupling of electrons) and remains, while the coupling between the nucleic magnetic moment and the electronic magnetic moment is strongly reduced. This effect is called Paschen-Back effect of the hyperfine interaction.

$$a = \frac{g_I \mu_K B_J}{\sqrt{J(J+1)}} \tag{10.98}$$

$$\Delta E_{PBHFS} = g_J \mu_B m_J B_0 + a m_J m_I - g_I \mu_K B_0 m_I \tag{10.99}$$

10.2.2 Electron spin resonance (EPR)

The technique of electron paramagnetic resonance (EPR) gives information on structure and dynamics of paramagnetic atoms and molecules. Especially the detection of triplet states (next chapter) is possible with EPR. Generally the molecules are diamagnetic and show no EPR signal. Paramagnetic molecules are

- Molecules with paramagnetic atoms such as Fe^{3+} or $[Fe(CN)_6)]^{3-}$ which are still paramagnetic with paired valence electrons.
- Radicals with an unpaired electron. There are stable radicals such as DPPH (Diphenyl-Picryl-Hydracyl) and radicals which can be created upon illumination or chemical reactions.
- Molecules in the triplet state. For some molecules the electronic ground state is a triplet state (O_2, NO, NO_2) and other molecules relax into a metastable triplet state after light excitation, such as naphthaline, chlorophylls, corroles, etc. The lifetime of the excited triplet states are in the range of 10^{-6}s.

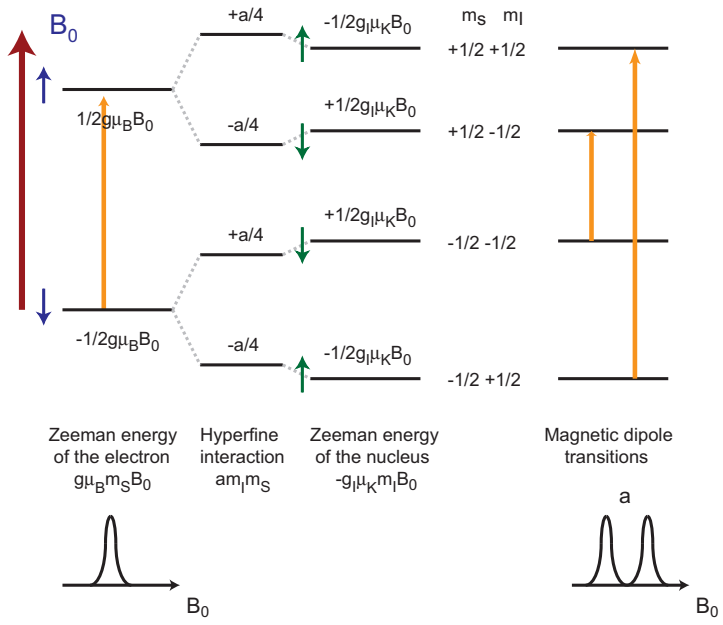


Abbildung 10.9. Hyperfine structure of a hydrogen atom in strong magnetic field and hyperfine structure of the EPR. Lower panel: left: EPR spectrum of a free electron; right: EPR spectrum of proton bound electron in a strong magnetic field.

An electron with the magnetic moment $|\overrightarrow{\mu_s}| = \mu_B g_S \sqrt{s(s+1)}$ has two possible orientations $m_s = \pm 1/2$ in a magnetic field $\overrightarrow{B}_0$ with energy difference ΔE

$$\Delta E = g_s \mu_B B_0 \tag{10.100}$$

Applying an electromagnetic field perpendicular to the magnetic field with the frequency $\nu = \mathbf{2.8026 \cdot 10^{10}} B_0 \frac{\mathrm{Hz}}{\mathrm{T}}$ can induce transitions between the spin levels of a 'free electron'. Selection rules for the magnetic dipole transitions are

$$\Delta m_s = \pm 1. \tag{10.101}$$

For magnetic fields in the range of 0.1T to 1T the frequencies are in the range of microwaves (frequencies of GHz). The **g-factor** of the paramagnetic electron can be determined by EPR. Generally the g-factor is a tensor and has different values along different axes. This is because of the interaction with the magnetic fields induced by the 'local currents' of the neighboring electrons (in chemical bonds). Thus, different chemical bonds can produce different chemical shifts. Nevertheless, the g-factor is often very similar to g_S (free electron).

More important are the contributions from the hyperfine interaction with the nuclear spin $\overrightarrow{I}$. The external and internal magnetic fields add up for the electron, where dipole-dipole interactions between nucleic and electronic magnetic dioples

are averaged out in solution (rotation of the molecules). The remaining part is the Fermi contact interaction

$$B_{loc} = B_0 + a m_I \tag{10.102}$$

$$h\nu = g\mu_B \left(B \pm \frac{a}{2}\right) \tag{10.103}$$

$$\Delta m_s = \pm 1, \quad \Delta m_I = 0 \tag{10.104}$$

In an experiment with N equivalent protons interacting with one electron (e.g.

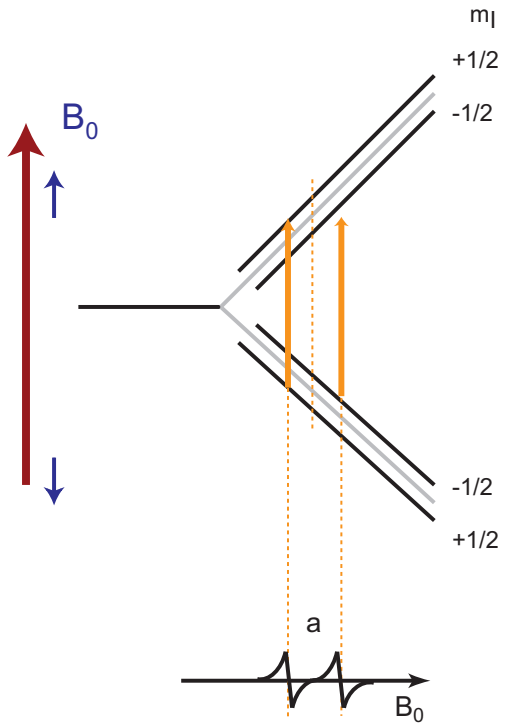


Abbildung 10.10. Hyperfine interaction of the magnetic moments of an electron and a nucleus ($I = 1/2$). In total there are four levels and two resulting transitions. Because of the experimental setup the measured signals are derivatives of absorption signals. They are separated by the hyperfine separation constant.

benzene-radical) we find $N + 1$ equivalent hyperfine lines with intensity ratios given by the Pascal triangle (1:6:15:20:15:6:1). Here we have to count all possible orientations of the equivalent spins.

Interaction between two different electron spins introduce a dipole-dipole interaction term H_D

$$H_D = g^2\mu_B^2 \left\{ \frac{\vec{S}_1 \cdot \vec{S}_2}{\vec{r}_{12}^{\,3}} - \frac{3(\vec{S}_1 \cdot \vec{r}_{12})(\vec{S}_2 \cdot \vec{r}_{12})}{\vec{r}_{12}^{\,5}} \right\} \tag{10.105}$$

which connects the distance between the two spins with its relative orientation to the interaction strengths. This dipole-dipole interaction term shifts the energy levels and the energetic positions of the resonance frequencies. The shifts are proportional to $\frac{1}{r^3}$ and give information about the averaged distances of the interacting electrons. This is especially useful in super-molecules such as proteins (photosystems).

10.2.3 Nuclear magnetic resonance (NMR)

In NMR experiments the Lamor frequency of the nuclear spins were measured. Since the magnetic moment of a nuclear spin is about 2000 times smaller than the magnetic moment of an electron, the magnetic field of the electron has to vanish at the nuclei of the investigated atoms and molecules. This is the case for atoms such as Hg, Cu, C, and S as well as for many molecules like H_2O, CaO, LiCl, CO_2, H_2, NH_3 and most biological molecules. The potential energy of the nucleic magnetic moment within the magnetic field $\overrightarrow{B}_0$ is

$$\begin{aligned} E_{NMR} &= -\overrightarrow{\mu}_I \cdot \overrightarrow{B}_0 && (10.106)\\ &= -g_I \mu_K B_0 m_I && (10.107)\\ \Delta m_I &= \pm 1 && (10.108)\\ |\Delta E_{NMR}| &= g_I \mu_K B_0 && (10.109)\\ \nu_{NMR} &= \frac{g_I \mu_K}{h} B_0 && (10.110)\\ \omega_{NMR} &= \frac{g_I \mu_K}{\hbar} B_0 = \gamma B_0 && (10.111)\\ \mu_I &= g_I I_{max} \mu_K && (10.112)\\ \nu &= 762.3 \frac{\mu_I}{I} B_0 \frac{[\text{Hz}]}{[\text{Gauss}]}. && (10.113) \end{aligned}$$

Equation (10.113) is the resonance condition for r.f. absorption in units of Hz / Gauss (1 Tesla $\cong$ 10 kGauss) leading to spin flip processes. The ratio of absorption ($N_1 \rightarrow N_2$) and emission depends on the population ratio given by Boltzmann statistics

$$\frac{N_1 - N_2}{N_1 + N_2} = \frac{1 - e^{-g_I \mu_K B_0/(k_B T)}}{1 + e^{-g_I \mu_K B_0/(k_B T)}} \approx \frac{g_I \mu_K B_0}{2\, k_B T}. \qquad (10.114)$$

Protons in different electronic environments experience different amounts of shielding σ, and the resonance absorption of light energy will occur at different values for the applied field or irradiating light frequency. These changes are referred to as **chemical shifts**.

$$\begin{aligned} B_{eff} &= B_0 - B_{induced} && (10.115)\\ B_{eff} &= B_0 - \sigma B_0 && (10.116)\\ h\nu &= g_I \mu_K B_{local} = g_I \mu_K B_0 (1 - \sigma). && (10.117) \end{aligned}$$

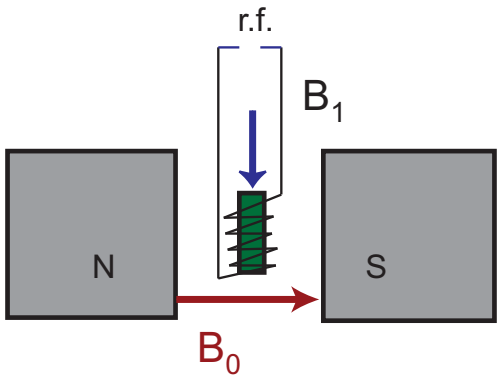


Abbildung 10.11. NMR setup; The sample (green) is positioned in a homogeneous and constant magnetic field B_0; perpendicular to B_0 an additional magnetic field B_1 is generated with a high frequency generator (r.f.); absorption of the r.f. field result in nuclear spin flips and in reducing the power of the induction coil, which is the measured quantity.

A possible NMR setup is presented in Fig. 10.2.3. In the static magnetic field along the z-axis, all nuclear magnetic spins precesses about the z-axis. Applying a NMR pulse of duration τ_p and rotation angle β with $\beta = -\gamma B_1 \tau_p$ rotates the equilibrium magnetization M_0 about the direction of the applied r.f. field B_1. For an r.f. field applied along the y-axis, the initial magnetization after the pulse is

$$M_x(0) = M_0 \sin\beta \tag{10.118}$$
$$M_y(0) = 0 \tag{10.119}$$
$$M_z(0) = M_0 \cos\beta. \tag{10.120}$$

The subsequent free induction decay can be described in terms of two components

$$M_x(t) = M_0 \sin(\beta)\cos(\Omega t)e^{-t/\tau_2} \tag{10.121}$$
$$M_y(t) = M_0 \sin(\beta)\sin(\Omega t)e^{-t/\tau_2} \tag{10.122}$$
$$M(t) = M_x(t) + iM_y(t) = M_0 \sin\beta e^{i\Omega t - t/\tau_2}. \tag{10.123}$$

The complex signal $s(t)$ obtained by simultaneous observation of both x- and y-components by quadrature detection, is directly proportional to the complex magnetization $M(t)$. This signal may be subjected to a complex Fourier trans-

formation

$$S(\omega) = \int_0^\infty s(t)e^{-i\omega t}d\omega \tag{10.124}$$

$$S(\omega) = v(\omega) + iu(\omega) \tag{10.125}$$

$$v(\omega) = M_0 \sin\beta\, a(\Delta\omega) \tag{10.126}$$

$$u(\omega) = -M_0 \sin\beta\, d(\Delta\omega) \tag{10.127}$$

$$\Delta\omega = \omega - \Omega \tag{10.128}$$

$$a(\Delta\omega) = \frac{1/\tau_2}{(1/\tau_2)^2 + (\Delta\omega)^2} \tag{10.129}$$

$$d(\Delta\omega) = \frac{\Delta\omega}{(1/\tau_2)^2 + (\Delta\omega)^2} \tag{10.130}$$

The equations (10.129) and (10.130) represent absorption and dispersion signals, respectively. Obviously, the maximum signal amplitude is obtained for a pulse rotation angle $\beta = \pi/2$. The transverse relaxation time τ_2 gives the width of the absorption spectra.

Some properties of NMR spectroscopy are

- The energy differences are very small of about 10^{-4} to 10^{-8} eV.
- In NMR magnetic dipole transitions were detected (not electric dipole transitions).
- The wavelength of the used radiation is big with respect to the sample dimensions. Thus, all nuclei can be excited coherently with the same phase.

As a result of the small energy differences a reference standard - the molecule tetramethylsilane $(CH_3)_4Si$ commonly abbreviated TMS - is measured in addition to the sample of interest. The detected resonance frequencies are expressed as δ in ppm

$$\delta_i = \frac{\nu_i - \nu_{TMS}}{\nu_0} \times 10^6 \text{ ppm}. \tag{10.131}$$

In addition to the chemical shift of protons, one can also measure the chemical shift of the carbons. In methane it is -2.1 ppm, and the chemical shift of the two equivalent CH_3 carbons in ethane is 5.9 ppm.

Direct magnetic dipole-dipole interaction between nuclei A and B change the magnetic field at the nucleus B. The magnetic field from the nucleus A at the position of nucleus B depend to the third power on the distance between the

nuclei, and depend on the orientation of the angle ϑ with respect to the vector $\overrightarrow{r}_{AB}$ and is given by

$$B_A = -\frac{\mu_0}{4\pi} g_I \mu_K m_I \frac{1}{r_{AB}^3}(1 - 3\cos^2\vartheta). \tag{10.132}$$

Assuming nucleus A to have spin 1/2, we have two orientations of the spin with respect to the external magnetic field $B_0 \pm B_A$ for parallel and antiparallel orientations. The nucleus B can see two different magnetic fields $B_0 + B_A$ or $B_0 - B_A$, leading to a resonance doublet of splitting $2B_A$. The same interaction is acting on the nucleus A. The energy splitting of the doublet is called spin-spin interaction J (see Fig. 10.2.3). In solid state samples the magnetic field B_A induced by spin-spin coupling can be as big as 10^{-4} T (for distances of 0.2 nm). In liquid samples the molecules rotate and move very fast, so that the term $(1-3\cos^2\vartheta)$ is averaged out and becomes zero. In super-molecules, such as proteins the rotation is very slow and the dipole-dipole interaction does not vanish. Therefore, in big molecules we can make use of the dipole-dipole interaction to extract distances and orientations from the spin-spin couplings. Indirect spin-spin coupling mechanisms also exist. They are smaller than the direct coupling mechanisms and can result from polarization of an electron magnetic moment by a nucleic magnetic moment and vice versa. If the chemical shift is the same for several identical

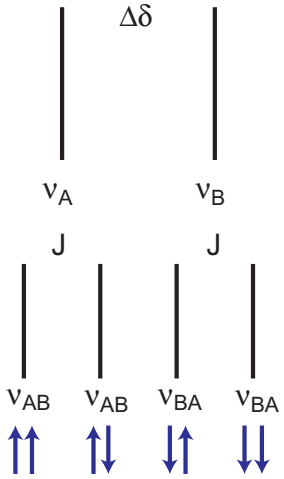


Abbildung 10.12. Splitting of NMR lines by spin-spin coupling J. The magnetic field of spin A influences the local field of spin B and vice versa. Here, $J < \delta$.

nuclei, then the nuclei are called **equivalent**. The two protons in a CH_2 group and the three protons in a CH_3 group are equivalent. They have identical resonance lines (single line in the spectrum). If both group are part of one molecule (CH_3CH_2OH), the different equivalent protons can interact with each other and the 3 protons of the CH_3 group split into 3 lines with intensity ratio 1:2:1, due to the coupling to the two protons of CH_2. The coupling of the 3 CH_3 protons

with one proton of the CH_2 introduce a splitting into two lines and the coupling with the other proton again into two lines with the same coupling constant J ($\rightarrow$ three lines). The two protons of the CH_2 group split into 4 lines with intensity ration 1:3:3:1. The direct and indirect spin-spin interactions do not depend on the external magnetic field. The spin-spin interaction can be isolated by measuring at different external field strengths.

The nuclear magnetic resonance technique is very successful in visualizing the consistence of a human body (**Magnetic Resonance Tomography**) and in resolving three dimensional structures of proteins on atomic resolution. The latter uses coherence spectroscopy by exciting with two resonance fields ω_1 and ω_2. For short times ($t < \tau_2$) the two spins can interact coherently with each other resulting in cross-peaks. The interaction strength gives information on the distance and orientations of the spins.

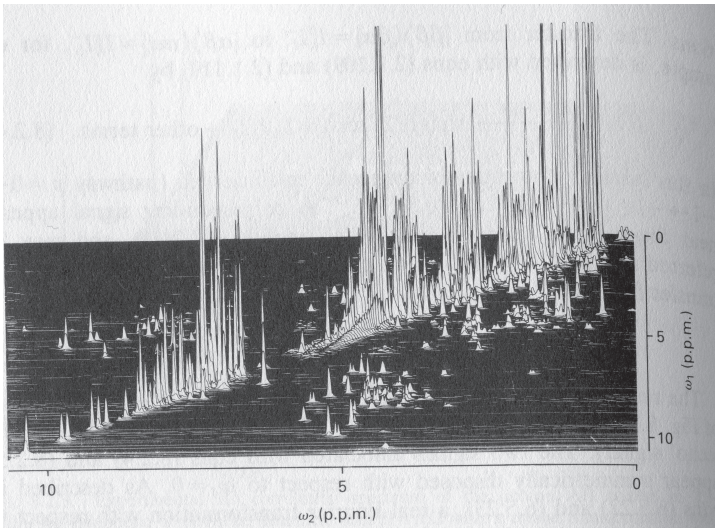


Abbildung 10.13. Homonuclear 2D correlation spectrum of basic pancreatic trypsin inhibitor (BPTI, with 58 amino-acid residues). Absolute mode.

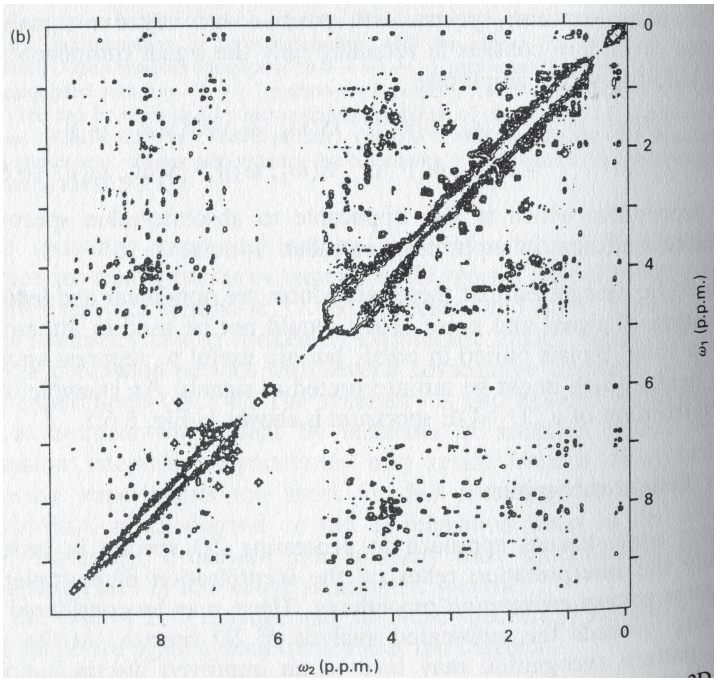


Abbildung 10.14. Absolute-value 2D NOE spectrum of the protein seminal inhibitor II A.

10.3 Lifetimes of excited states

As we saw in the sections above, most experiments deal with dipole approximation or dipole interactions. We learned that the intensity of a transition between a pair of states f and i is proportional, in the dipole approximation, to the quantity $|\overrightarrow{r}_{fi}|^2$. The relative intensities of a series of transitions from a given initial state i to various final states f are determined by the quantity f_{fi} called **oscillator strength**

$$f_{fi} = \frac{2m\omega_{fi}}{e\hbar}|\overrightarrow{r}_{fi}|^2 \tag{10.133}$$

with $\omega_{fi} = (E_f - E_i)/\hbar$. Note, that $f_{ki} > 0$ for absorption and $f_{ki} < 0$ for emission processes. The oscillator strengths obey the sum rule, due to Thomas, Reiche and Kuhn

$$\sum_f f_{fi} = 1 \tag{10.134}$$

where the sum is over all states, including the continuum. The transition rates for spontaneous emission in the dipole approximation are given in terms of oscillator strengths by

$$W^s_{fi} = \frac{2\hbar\alpha}{mc^2}\omega^2_{fi}|f_{fi}|. \tag{10.135}$$

For hydrogenic atoms the oscillator strengths and transition probabilities decrease as the principal quantum number n of the upper level increases.

10.3.1 Atomic lifetimes

If $N(t)$ atoms are in an excited state i at a particular time t, the rate of change of $N(t)$ is

$$\dot{N}(t) = -N(t)\sum_f W^s_{fi} \tag{10.136}$$

where W^s_{fi} is the transition rate for spontaneous emission and the sum is over all states f, of lower energy, to which decay is allowed by the selection rules. On integration, $N(t)$ can be expressed by

$$N(t) = N(t=0)e^{-t/\tau_i}. \tag{10.137}$$

where τ_i is called the lifetime of level i and is

$$\frac{1}{\tau_i} = \sum_f W^s_{fi}. \tag{10.138}$$

For example, the lifetime of the 2p level of a hydrogenic atom is seen to be $\tau = \frac{0.16}{Z^4}10^{-8}$s. For higher nucleic charges is

$$\tau(Z) = \frac{1}{Z^4}\tau_{Z=1}. \tag{10.139}$$

Average oscillator strengths for some transitions in hydrogenic atoms and ions are shown below

Initial level	Final level	n = 1	n = 2	n = 3	n = 4	$\sum_{n=5}^{\infty}$	Continuum spectrum
1s	np	-	0.416	0.079	0.029	0.041	0.435
2s	np	-	-	0.435	0.103	0.111	0.351
2p	ns	-0.139	-	0.014	0.003	0.003	0.008
2p	nd	-	-	0.696	0.122	0.109	0.183

The lifetime of some levels of atomic hydrogen (in 10^{-8}s) are

Level	2p	3s	3p	3d	4s	4p	4d	4f
lifetime	0.16	16	0.54	1.56	23	1.24	3.65	7.3

10.4 Density operator

The density matrix of a pure quantum state $|\psi\rangle$ is defined as:

$$\rho = |\psi\rangle|\langle\psi|, \tag{10.140}$$

when we expand ψ in a basis $|n\rangle$, we find

$$\langle\psi| = \sum_n c_n\langle n| \tag{10.141}$$

$$|\psi\rangle = \sum_m c_m^*|m\rangle \tag{10.142}$$

$$\rho = \sum_{n,m} c_n c_m^*|n\rangle\langle m| \tag{10.143}$$

$$\rho_{n,m} \equiv \langle n|\rho|m\rangle = c_n c_m^*. \tag{10.144}$$

The expectation value of an operator A is defined as:

$$\langle A\rangle \equiv \langle\psi|A|\psi\rangle = \sum_{n,m}\rho_{nm}A_{nm}. \tag{10.145}$$

With the definition of the trace we have

$$Tr(A\rho) = \sum_n (A\rho)_{nn} = \sum_n(\sum_m A_{nm}\rho_{mn}) \tag{10.146}$$

$$Tr(A) = \sum_n A_{nn} \tag{10.147}$$

$$\langle A\rangle = Tr(A\rho) \tag{10.148}$$

The trace is invariant to unitary transformations (i.e. invariant to basis transformations). The time evolution of the density operator is given by

$$\frac{d}{dt}\rho = \frac{d}{dt}(|\psi\rangle\langle\psi|) = \left(\frac{d}{dt}|\psi\rangle\right)\langle\psi| + |\psi\rangle\left(\frac{d}{dt}\langle\psi|\right). \tag{10.149}$$

Inserting this into the SE we find

$$\begin{aligned}
\frac{d}{dt}|\psi\rangle &= -\frac{i}{\hbar}H|\psi\rangle && (10.150)\\
\frac{d}{dt}\langle\psi| &= +\frac{i}{\hbar}H\langle\psi| && (10.151)\\
\frac{d}{dt}\rho &= -\frac{i}{\hbar}H|\psi\rangle\langle\psi| + \frac{i}{\hbar}|\psi\rangle\langle\psi|H && (10.152)\\
&= -\frac{i}{\hbar}H\rho + \frac{i}{\hbar}\rho H && (10.153)\\
\Rightarrow \frac{d}{dt}\rho &= -\frac{i}{\hbar}[H,\rho]. && (10.154)
\end{aligned}$$

Equation (10.154) is called Liouville von Neumann equation and describes the time evolution of the system. Since the probability P_ϕ of finding the system in the state ϕ is given by $P_\phi = \langle\phi|\rho|\phi\rangle$ (if ϕ is normalized), two systems are identical if they have the same density operator.

The density operator can describe *pure states* $\rho = |\psi\rangle\langle\psi|$, but also mixed states. Equations

$$\frac{d}{dt}|\psi\rangle = -\frac{i}{\hbar}H|\psi\rangle \Leftrightarrow \frac{d}{dt}\rho = -\frac{i}{\hbar}[H,\rho] \tag{10.155}$$

are identical, as long as ρ is the density matrix of a pure state. However, in general we have statistical ensembles and there is no way to write down a wave function of a statistical average, but we can write down the density matrix of a statistical average. Let P_n be the probability of a system being in a pure state $|\psi\rangle$, then the density matrix is defined as:

$$\begin{aligned}
\rho &= \sum_n P_n|\psi\rangle\langle\psi| && (10.156)\\
\text{with } P_n &\geq 0 && (10.157)\\
\sum_n P_n &= 1 && (10.158)\\
\rho_{nm} &= \rho^*_{mn} && (10.159)\\
\rho_{nn} &= \geq 0 && (10.160)\\
Tr(\rho) &= 1 && (10.161)
\end{aligned}$$

Let for example $|\psi\rangle$ be one of the basis states

$$|\psi\rangle = |a\rangle \tag{10.162}$$

$$\rightarrow \rho = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} \tag{10.163}$$

$$\rho = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \tag{10.164}$$

$$\text{or} \quad |\psi\rangle = |b\rangle \tag{10.165}$$

$$\rightarrow \rho = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \end{pmatrix} \tag{10.166}$$

$$\rho = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \tag{10.167}$$

and a coherent superposition state of both (which is still a pure state) is

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|a\rangle + |b\rangle) \tag{10.168}$$

$$\Rightarrow \rho_{nm} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \end{pmatrix} \tag{10.169}$$

$$= c_n c_m^* = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}. \tag{10.170}$$

On the other hand, for a statistical average between both states with $P_1 = P_2 = 0.5$ we get

$$\rho = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}. \tag{10.171}$$

The diagonal elements are the same in both cases, but the off-diagonal elements which describe the coherence between both states are different. Note, there is no wave function $|\psi\rangle$ which would give a density matrix as in equation (10.171). Assume we have a Hamilton operator with eigenstate basis so that we have

$$H = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} \tag{10.172}$$

$$\begin{aligned} \frac{d}{dt} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} &= -\frac{i}{\hbar} \left[\begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} - \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} \right] \\ &= -\frac{i}{\hbar} \begin{pmatrix} 0 & (\epsilon_1 - \epsilon_2)\rho_{12} \\ (\epsilon_2 - \epsilon_1)\rho_{21} & 0 \end{pmatrix} \end{aligned} \tag{10.173}$$

$$\dot{\rho}_{11} = 0 \quad \Rightarrow \quad \rho_{11}(t) = \rho_{11}(0) \tag{10.174}$$

$$\dot{\rho}_{22} = 0 \quad \Rightarrow \quad \rho_{22}(t) = \rho_{22}(0) \tag{10.175}$$

$$\dot{\rho}_{12} = -\frac{i}{\hbar}(\epsilon_1 - \epsilon_2)\rho_{12} \quad \Rightarrow \quad \rho_{12}(t) = e^{-i\frac{\epsilon_1 - \epsilon_2}{\hbar}t}\rho_{12}(0) \tag{10.176}$$

$$\dot{\rho}_{21} = -\frac{i}{\hbar}(\epsilon_2 - \epsilon_1)\rho_{21} \quad \Rightarrow \quad \rho_{21}(t) = e^{+i\frac{\epsilon_2 - \epsilon_1}{\hbar}t}\rho_{21}(0). \tag{10.177}$$

The diagonal elements are stationary in time (as expected) while the off-diagonal elements oscillate with the frequency splitting $\omega = \Delta\epsilon/\hbar = (\epsilon_1 - \epsilon_2)/\hbar$. In spectroscopic experiments the dephasing of an ensemble of molecules is observed. The simplest approach to describe dephasing Γ (Γ real and positive) phenomenologically is:

$$\begin{aligned}
\dot{\rho}_{12} &= -\frac{i}{\hbar}(\epsilon_1 - \epsilon_2)\rho_{12} - \Gamma\rho_{12} && (10.178)\\
\rho_{12}(t) &= e^{-i\frac{\epsilon_1-\epsilon_2}{\hbar}t}e^{-\Gamma t}\rho_{12}(0) && (10.179)\\
\dot{\rho}_{21} &= \frac{i}{\hbar}(\epsilon_2 - \epsilon_1)\rho_{21} - \Gamma\rho_{21} && (10.180)\\
\rho_{21}(t) &= e^{i\frac{\epsilon_2-\epsilon_1}{\hbar}t}e^{-\Gamma t}\rho_{21}(0). && (10.181)
\end{aligned}$$

In the wave function picture it is not possible to describe dephasing. If we introduce an interaction with an optical light field $E(t)$:

$$H = H_0 + \overrightarrow{E}(t)\cdot\overrightarrow{\underline{\mu}} \simeq H_0 + \overrightarrow{E}_0\left(e^{i\omega t} + e^{-i\omega t}\right)\cdot\overrightarrow{\underline{\mu}}, \qquad (10.182)$$

and we get

$$\begin{aligned}
H &= \epsilon_1|a\rangle\langle a| + \epsilon_2|b\rangle\langle b| - \overrightarrow{\underline{\mu}}\cdot\overrightarrow{E}(t)(|a\rangle\langle b| + |b\rangle\langle a|) && (10.183)\\
H &= \begin{pmatrix} \epsilon_1 & -\overrightarrow{\underline{\mu}}\cdot\overrightarrow{E}(t) \\ -\overrightarrow{\underline{\mu}}\cdot\overrightarrow{E}(t) & \epsilon_2 \end{pmatrix} && (10.184)
\end{aligned}$$

Nonlinear Optics:
The electric displacement $\overrightarrow{D}$ and the macroscopic polarization $\overrightarrow{P}$ is given by

$$\begin{aligned}
\overrightarrow{D} &= \varepsilon_0\overrightarrow{E} + \overrightarrow{P} && (10.185)\\
\overrightarrow{P} &= \varepsilon_0\left(\chi^{(1)}\overrightarrow{E} + \chi^{(2)}\overrightarrow{E}\,\overrightarrow{E} + \chi^{(3)}\overrightarrow{E}\,\overrightarrow{E}\,\overrightarrow{E} + \ldots\right) && (10.186)\\
\overrightarrow{P}(t) &= Tr(\overrightarrow{\underline{\mu}}\rho(t)) \equiv \langle\overrightarrow{\underline{\mu}}\rho(t)\rangle, && (10.187)
\end{aligned}$$

and for the example of a two level system we get

$$\begin{aligned}
\underline{\mu} &= \begin{pmatrix} 0 & \underline{\mu}_{12} \\ \underline{\mu}_{21} & 0 \end{pmatrix} && (10.188)\\
\langle\underline{\mu}\rho(t)\rangle &= \rho_{12}\underline{\mu}_{21} + \rho_{21}\underline{\mu}_{12} && (10.189)\\
P^{(n)}(t) &= \langle\underline{\mu}\rho^{(n)}(t)\rangle && (10.190)
\end{aligned}$$