Course Spectroscopy

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The course ’Spectroscopy’ is dedicated mainly to students of physics and chemistry but also suitable for students from other disciplines such as biology or materials engineering where spectroscopic techniques are frequently used. It covers a broad range of spectroscopic techniques from the very low frequency end (NMR) to the very high frequency end (Mößbauer spectroscopy) of the electromagnetic spectrum. Special emphasis is set on the general physical principles of the interaction between electromagnetic radiation and matter common to all spectroscopies. In the later chapters, individual techniques for a given frequency or wavelength range are presented. Those just present a brief overview about the specialties and possibilities for application to a given problem in, e. g., chemical structure analysis. For further details, special textbooks should be studied. Literature as well as general questions of recapitulation are given at the end of each chapter.

I’m especially dedicated to Prof. Freude who developed this course and of whom I took the original manuscript that I adapted to my style.

Marko Bertmer
Chapter 1

Introduction

1.1 Definition

Origin of name:

latin: *spectrum* = image in the soul

greek: *skopein* = to look

Common explanation: a spectrum (pl. spectra) is a plot of intensity (in arbitrary units) as a function of frequency, wavelength or energy.

These are all directly related to each other and can be interconverted:

\[
E = h\nu
\]

\[
E = \frac{hc}{\lambda}
\]

\[
c = \nu\lambda
\]

(E: energy, dimension Joule [J], sometimes given in electron volt (eV); 1 eV = 1.602·10^{-19} J; \(\nu\): frequency, dimension Hertz [Hz = s^{-1}]; \(\lambda\): wavelength, dimension meter [m])

Herein the fundamental constants: \(h = 6.6260689633·10^{-34}\) Js (Planck’s constant) and \(c = 299792458\) ms^{-1} (speed of light in vacuum) are used.

Notice: the term ‘spectroscopy’ is not always use in this strict sense (as it should be done). As an example, the term ‘mass spectroscopy’ is not correct, ‘mass spectrometry’ is better though might also cause misinterpretation. There, a ‘spectrum’ corresponds to intensity as a function of particle mass. However, the term is commonly used.
1.2 Historical development

A historical reflection is always incomplete, we just focus on a few selected points.

- 60 B.C.: Titus Carus Lucretius (often called the ‘intellectual father’ of IR spectroscopy) postulated the existence of radiative heat around a fire flame [1]

- 1666: Isaac Newton (Cambridge) used a glass prism to split sunlight into its different colors; was the first to use the expression ‘spectrum’ [2] Newton was probably the first to go from a description and speculation about observations in nature to a ‘scientific’ approach using exact measurements and planning specific experiments.

- 1686: Edmé Mariotte experimentally demonstrated the hypothesis of Lucretius. In his experiment the temperature of the heat image by a candle focused by a metal mirror decreased after putting a glass plate between candle and mirror. [3]

- 1800: Frederick William Herschel ‘detected’ the infrared. With a glass prism he directed sunlight into a darkened room and used two thermometers to measure the temperature at two points. There he observed that ‘after’ the red area (which we call nowadays the infrared, ‘infra’ Latin for below) there was still a temperature effect. [4]

- 1801 Johann Wilhelm Ritter ‘found’ the ultraviolet range (‘ultra’ Latin for beyond) by observing that the darkening effect of silver chloride did not end at the violet end of the visible spectrum. [5]

- 1802 William Hyde Wollaston observed black ‘lines’ in the continuous spectrum of the sun. [6]

- 1817 Joseph von Fraunhofer identified that these ‘lines’ (see Fig. 1.1) were caused by selective absorptions in the photosphere or atmosphere and labeled them with capital letters. [7] The most prominent one is the Na-D line (588.9 nm) still used as reference today. This is also the one responsible for the yellow color in a candlelight.
1.3 Atomic spectra of hydrogen

Ångström also measured the lines of atomic hydrogen. In 1885 Johann Jakob Balmer found an (empirical) formula that explained the experimental results [10]:

$$\lambda = H \frac{m^2}{m^2 - 4}$$  \hspace{1cm} (1.4)

with \(m\) as an integer number from 3 to 11 and \(H = 364.56\) nm being a constant.

A further improvement came from Janne Robert Rydberg 1889 [11]:

$$\tilde{\nu} = R_H \left( \frac{1}{n'^2} - \frac{1}{n''^2} \right)$$  \hspace{1cm} (1.5)

with the Rydberg constant \(R_H = 109677.58\) cm\(^{-1}\). For the so-called Balmer series \(n' = m > 2\) and \(n'' = 2\).

This equation could also explain the later found series:
The electronic transitions (see chapter 2.2) for the hydrogen atom are shown schematically in Figure 1.3.

According to Bohr’s atomic model and quantum mechanics, \( n' \) and \( n'' \) are referred to as shells (e.g. K-shell) or the first (principal) quantum number, respectively (see chapter 3).
1.4 Electromagnetic spectrum

A spectrum is the consequence of the interaction of an electromagnetic wave with matter of various type like atoms, molecules, and nuclei or electron spins.

The full electromagnetic spectrum is shown in Fig. 1.4 together with the names for given ranges. Additionally, wavelength and frequency are indicated.

In general, it doesn’t matter if one expresses the spectrum as a function of frequency, wavelength or energy (as discussed above). However, historically or because of practial reasons for some ranges one dimension is used predominantly, e. g. in the optical range nanometer is used as unit whereas NMR and ESR use frequency and Mößbauer spectroscopy uses energy (mainly expressed in keV).

One additional unit is often used in infrared spectroscopy: the wavenumber. The
Figure 1.4: The full electromagnetic spectrum.

definition is given as

\[ \tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} \]  

(1.6)

with the dimension cm\(^{-1}\).

This course starts with the discussion of features common to all spectroscopic techniques (chapter 2 and 3) before going into details for a specific experimental technique (chapters 4 to 8) discussed in the order of increasing frequency.

1.5 The Experimental Scientist

Just as an illustration and maybe a guideline for future (or current) scientists, the general development of scientific progress is given. This is the personal opinion of the author and might not be identical for everyone.

Based on the first experiments by Newton, we would characterize the general strategy of an experimental scientist in the following context:

- Observations in nature [laboratory]
- Planning of experiments to prove or disprove certain assumptions that explain the observed effects
1.6. LITERATURE

- Trying to understand the observations and creating a theory [due to the complexity nowadays this is often done by someone else]

- Test theory with new experiments that prove or disprove this theory

- Use theory for predictions on other subjects or for further experiments

This procedure is something we should follow. Keep in mind that any theory is valid as long as no experiment can prove that it is wrong.

1.6 Literature

There are numerous textbooks for the individual experimental techniques, a selection will be given at the end of each chapter. General textbooks on spectroscopy that treat the whole electromagnetic spectrum are rare (if existing at all). Nevertheless, J. M. Hollas, *Modern Spectroscopy*, John Wiley & Sons, Chichester, 1992 (also other editions exist).

can be used as a starting point. The book contains some general, common feature description, though it is not extensive and detailed enough for us. It can be used as a starting point. Later on it focusses mainly on electronic, vibrational, and rotational spectroscopy

Therefore, for further explanations we often refer to physics textbooks that provide more details such as:


Other textbooks apply as well. See also the individual literature at the end of each chapter.
1.7 Questions for Recapitulation

1. What was/is silver chloride used for and what is the chemical reaction by interaction with light?

2. Why was the Brackett series \((n = 2)\) the first to be observed for the hydrogen atom and not the one for \(n = 1\)?

3. Calculate the wavelengths for the hydrogen atom transitions in the different series up to the 8\(^{th}\) energy level and compare it to the values given in Fig. 1.3. Express the values also in units of energy.

1.8 References


Chapter 2

Absorption and Emission of Radiation

2.1 Electromagnetic Radiation

Please keep in mind that there is no principle difference between an electromagnetic wave and a light wave. Often a light wave is confined to the visible part of the electromagnetic spectrum.

As the name indicates, an electromagnetic wave contains two components. Fig. 2.1 represents this phenomenon for a linearly polarized wave. The electric field $\vec{E}$ and the magnetic field $\vec{H}$ are perpendicular to each other and also perpendicular to the propagation of the wave. In the figure, the propagation axis is $x$ and $\vec{E}$ is in the $x$-$y$ plane whereas $\vec{H}$ is in the $x$-$z$ plane. Both $E$ and $H$ have the same frequency $\nu$ and the same wave vector $k$. Since the argument of the cosine (or sine) function has to be dimensionless, $k$ has the dimension $m^{-1}$. Both $\vec{E}$ and $\vec{H}$ can be described as a function of space ($x$ in this case) and time ($t$):

$$E_y = A^E_y \cos(k_x x - 2\pi \nu t) \quad (2.1)$$

$$H_z = A^H_z \cos(k_x x - 2\pi \nu t) \quad (2.2)$$

$$k = 2\pi/\lambda; \text{ compare to } \omega = 2\pi/\lambda$$

Electromagnetic waves are transversal waves since $\vec{E}$ and $\vec{H}$ oscillate perpendicular to the propagation direction. A typical example is a horizontal rope fixed at one end and. A given point on the rope does not change its position with respect
to the propagation direction but only its height. This can be understood as the amplitude and phase of the wave.

There are also longitudinal waves, the most prominent ones are sound waves. Here, pressure differences are responsible for the wave and the propagation is always connected with the movement of matter.

Water waves are complicated waves that are in most cases a combination of both longitudinal and transverse components.

Next to $\vec{E}$ and $\vec{H}$ other terms are frequently used. The terms $\vec{D}$ (dielectric displacement) and $\vec{P}$ (induced electric polarization) are related to the electric field $\vec{E}$ by:

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon_r \varepsilon_0 \vec{E} = \varepsilon_0 (1 + \chi_e) \vec{E}$$  \hspace{1cm} (2.3)

Here $\varepsilon_0$ refers to the permittivity of a vacuum ($\varepsilon_0 = 8.854187817 \cdot 10^{-12} Fm^{-1}$) and $\varepsilon_r$ is the relative dielectric constant (dimensionless). $\chi_e$ is the electric susceptibility.

A similar relation exists for the magnetic induction $\vec{B}$ and the magnetization $\vec{M}$ with respect to $\vec{H}$:

$$\vec{B} = \mu_0 (\vec{H} + \vec{M}) = \mu_r \mu_0 \vec{H} = \mu_0 (1 + \chi) \vec{H}$$  \hspace{1cm} (2.4)

with the permeability of a vacuum ($\mu_0 = 4\pi \cdot 10^{-7} \frac{Vs}{Am}$) and $\mu_r$ the relative permeability constant.

Keep in mind that $\vec{H}$ and $\vec{M}$ have the same dimension, while $\vec{E}$ and $\vec{P}$ do not!
\subsection{Absorption and Emission}

The speed of an electromagnetic wave in a medium different than vacuum can be obtained from the simple relation:

\[ c = \lambda \nu = \frac{1}{\sqrt{\varepsilon_r \varepsilon_0 \mu_r \mu_0}} = \frac{c_0}{\sqrt{\varepsilon_r \mu_r}} \]  \hfill (2.5)

In vacuum $\varepsilon_r = \mu_r = 1$.

In most cases the interaction of matter with the electric field is relevant for spectroscopic techniques. Just for magnetic resonance techniques (NMR and ESR) the magnetic field interaction has to be considered.

The effects of the interaction of electromagnetic radiation with matter (particles, atoms, molecules, electrons, spins, ...) can be best explained according to the diagram shown in Fig. 2.2.

![Energy Diagram](image)

\textbf{Figure 2.2:} Energy diagram for absorption, induced (stimulated), and spontaneous emission.

Let’s consider a two-energy level system $E_1$ and $E_2$ with the former being the lower energy state. This could be the energetic ground state but doesn’t have to be. The populations of the energy levels are assigned as $N_1$ and $N_2$, respectively.

Three processes have to be distinguished, with the spontaneous emission being the only one that occurs without external influence. A particle at energy $E_2$ moves to the lower energy state $E_1$ and therefore emits electromagnetic radiation according to the relation
\[ \Delta E = E_2 - E_1 = h\nu \] (2.6)

This is also known as the resonance condition.

The two other processes - absorption and stimulated emission - need external stimulation by electromagnetic radiation of appropriate energy \( E = h\nu \). In the first case, the energy is absorbed so that a particle can go from energy level 1 to energy level 2. Alternatively, the electromagnetic wave stimulated the emission of a second wave of identical energy under which a particle goes from energy level 2 to energy level 1.

The time dependent changes of the two populations can be described individually for the three processes as follows:

\[
\frac{dN_2}{dt} = N_1 B_{12} \rho_v \quad \text{absorption} \quad (2.7)
\]
\[
\frac{dN_2}{dt} = -N_2 B_{21} \rho_v \quad \text{stimulated emission} \quad (2.8)
\]
\[
\frac{dN_2}{dt} = -N_2 A_{21} \quad \text{spontaneous emission} \quad (2.9)
\]

\( \rho_v \) represents the spectral energy density. \( A \) and \( B \) are the Einstein coefficients.

In equilibrium, the change of populations is 0, \( dN_2 = dN_1 \), or

\[ \frac{dN_2}{dt} = (N_1 B_{12} - N_2 B_{21}) \rho_v - N_2 A_{21} = 0 \] (2.10)

Additionally, the populations of the two energy levels are related by the Boltzmann distribution:

\[ \frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\frac{\Delta E}{kT}} \] (2.11)

\( g_i \) describe the degeneracy of the energy levels, which we assume to be 1 in this case.

From this we obtain together with \( B_{12} = B_{21} \) (see chapter 2.3) the relation between the coefficients

\[ \frac{A_{21}}{B_{21}} = \frac{N_1 - N_2}{N_2} \rho_v \] (2.12)

### 2.3 Black Body Radiation

To get further insight into the importance of the Einstein coefficients and the derivation of radiation laws, we discuss the principle of the black body. It is an idealized
2.3. BLACK BODY RADIATION

A black body absorbs all electromagnetic radiation at any wavelength completely. Because of this, a direct relation between the temperature of the black body and the emitted wavelengths can be obtained (objects that do not behave like a black body are often referred to as gray bodies, in the radiation laws this can be corrected for by including a proportionality factor $\epsilon$ with values between 0 and 1, with the latter representing a black body).

Let’s consider the diagram in Fig. 2.3 representing the emitted energy density of a black body as a function of wavelength for different temperatures.

![Figure 2.3: Wavelength dependence of emitted energy density.](image)

1893 Wilhelm Wien observed a simple empirical relation between the wavelength with maximum energy density $\lambda_{\text{max}}$ and temperature $T$:

$$\lambda_{\text{max}} * T = 2.9 \cdot 10^{-3} \text{mK}$$

(2.13)

This relation also sets the basis for the color temperature often given for light
CHAPTER 2. ABSORPTION AND EMISSION OF RADIATION

bulbs. With common temperatures on earth $T = 300K$ the maximum lies in the infrared (10 $\mu$m) whereas the IR is often referred to as heat radiation though this is only true for low temperatures. For the (surface) temperature of the sun ($T = 5800K$) the maximum lies in the visible range ($\lambda_{max} = 500$ nm).

Later on, 1896 Wien described his radiation law more specifically:

$$\rho_V = \frac{8\pi h \nu^3}{c_0^3} e^{-\frac{h\nu}{kT}}$$  \hspace{1cm} (2.14)

with $\rho_V$ describing the spectral energy density of a black body. Originally, Wien had a more empirical equation with the spectral specific extinction

$$\Phi_\lambda = \frac{C}{\lambda^3} e^{-\frac{hc}{kT}}$$  \hspace{1cm} (2.15)

which can be transformed into the upper equation with the constants $C = \frac{2\pi h c_0^2}{c}$ and $c = \frac{hc}{k_B}$, $k_B$ being Boltzmann’s constant.

Additionally, 1900 Rayleigh [1] and Jeans [2] derived an equation based on classical assumptions:

$$\rho_V = \frac{8\pi \nu^2 kT}{c_0^3}$$  \hspace{1cm} (2.16)

The differences between Wien’s and Rayleigh-Jeans radiation laws are described in Fig. 2.4.

The differences are obvious. Especially, the Rayleigh-Jeans law runs into problems in the UV range, known as the UV catastrophe [3]: at higher frequency (lower wavelength) more and more radiation would be emitted. The Rayleigh-Jeans approach started using a classical oscillator approach (for oscillator see chapter 6). It assumes that an oscillator emits at all frequencies, with the oscillations being more intensive as energy increases.

To overcome this problem, Max Planck 1900 defined his radiation law:

$$\rho_V = \frac{8\pi h \nu^3}{c_0^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$  \hspace{1cm} (2.17)

Though, mathematically, he ’just’ added a -1 in the denominator, his physical explanation was different from Rayleigh and Jeans. Based on his quantization idea ($E = h\nu$), electronic excitations are only active according to a certain energy and not all are active in general. The resulting curve of Planck’s radiation law is also included in Fig. 2.4. It can be seen that Wien’s radiation law is correct for high
2.3. BLACK BODY RADIATION

Figure 2.4: Representation of the different radiation laws; green: Rayleigh-Jeans law, red: Wien radiation law, blue: Planck radiation law.

frequencies (and low temperatures), while the Rayleigh-Jeans law is correct at low frequencies (and high temperatures). Mathematically, this can be demonstrated as follows:

For high frequencies, \( h\nu \gg kT \) and therefore \( e^{\frac{h\nu}{kT}} \gg 1 \) which leads to Wien’s radiation law. On the other hand at low frequencies, \( h\nu \ll kT \) and with the use of the Taylor expansion (see Appendix 10.1) the exponential function can be expressed as \( e^{\frac{h\nu}{kT}} \approx 1 + \frac{h\nu}{kT} \) and that leads to

\[
\rho_V = \frac{8\pi h\nu^3}{c_0^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} \Rightarrow \frac{8\pi h\nu^3}{c_0^3} \frac{1}{1 + \frac{h\nu}{kT} - 1} \Rightarrow \frac{8\pi h\nu^3 kT}{c_0^3} \frac{1}{h\nu} \Rightarrow \frac{8\pi h\nu^2 kT}{c_0^3} \tag{2.18}
\]

which is the Rayleigh-Jeans law.

For completeness, the Stefan-Boltzmann law is given.

\[
P = \sigma T^4 \tag{2.19}
\]

It states that the emitted radiofrequency power is proportional to the temperature to the fourth power with \( \sigma \) being a material constant. It was experimentally found by Josef Stefan in 1878 and derived by Ludwig Eduard Boltzmann 1884 from the laws of thermodynamics.
In the following, we will relate the Einstein coefficients defined in chapter 2.2 to derive Planck’s radiation law. We start with the situation as in Fig. 2.2 and rewrite the changes of population due absorption and emission of electromagnetic radiation:

\[ -dN_1 = B_{12} \rho V N_1 dt \quad (2.20) \]
\[ -dN_2 = (B_{21} \rho V + A_{21}) N_2 dt \quad (2.21) \]

In equilibrium \( dN_1 = dN_2 \) and we obtain

\[ \frac{N_2}{N_1} = \frac{B_{12} \rho V}{B_{21}} \rho V + A_{21} \quad (2.22) \]

Additionally, the Boltzmann equation is valid

\[ \frac{N_2}{N_1} = e^{-\frac{h \nu}{kT}} \quad (2.23) \]

which brings us to

\[ \frac{B_{12} \rho V}{B_{21} \rho V + A_{21}} = e^{-\frac{h \nu}{kT}} \quad (2.24) \]
\[ \Leftrightarrow \rho V = \frac{A_{21}}{B_{12} e^{\frac{h \nu}{kT}} - B_{21}} \quad (2.25) \]

At infinite temperature, the spectral energy should also be infinite, meaning \( B_{12} = B_{21} \).

At low frequencies (using Taylor-expansion as above), we therefore obtain

\[ \rho V = \frac{A_{21} kT}{B_{21} h \nu} \quad (2.26) \]

which together with the Rayleigh-Jeans law (valid at low frequencies) yields

\[ \frac{A_{21}}{B_{21}} = \frac{8 \pi h \nu^3}{c_0^3} \Leftrightarrow A_{21} = B_{21} \frac{8 \pi h \nu^3}{c_0^3} \quad (2.27) \]

which is correct for any arbitrary relation between \( h \nu \) and \( kT \).

Introducing this in equation 2.25 leads to

\[ \rho V = \frac{B_{21} \frac{8 \pi h \nu^3}{c_0^3}}{B_{21} e^{\frac{h \nu}{kT}} - B_{21}} = \frac{8 \pi h \nu^3}{c_0^3} \frac{1}{e^{\frac{h \nu}{kT}} - 1} \quad (2.28) \]

which is Planck’s radiation law.
2.4. LIFETIME AND LINEWIDTH

With that, we obtain a relationship between the spontaneous and induced emission probability as

$$\frac{A_{21}}{B_{21} \rho V} = \frac{h \nu}{kT},$$  \hfill (2.29)

which states that spontaneous emission become more probable at higher frequencies.

Though the black body is an idealized thing, its use is widespread. Especially, as can be seen in Fig. 2.5, even the sun can be very well approximated as being a black body.

![Figure 2.5: Spectral energy density of the sun in comparison to the calculated black body radiation.](image)

Figure 2.5: Spectral energy density of the sun in comparison to the calculated black body radiation.

The shape of the curves is almost identical - especially for the extraterrestrial radiation - with the terrestrial sun spectrum containing 'dips' due to atmospheric absorption.

2.4 Lifetime and Linewidth

Lifetime and linewidth are characteristic values in spectroscopy and yield detailed information about atoms and molecules. The lifetime always means the lifetime of an excited state without interaction with electromagnetic radiation that is ended
by spontaneous emission (the lifetime of a ground state being principally infinite in this situation). To derive a relation for the lifetime we start at the initial condition $t = 0$ with an initial population $N_2 = N_0$.

$$\Rightarrow -dN_2 = A_{21}N_2 dt \quad (2.30)$$

$$\Rightarrow N_2(t) = N_0 e^{-A_{21}t} \quad (2.31)$$

Remember that only spontaneous emission is considered.

This exponential decaying function states that every particle has an individual lifetime between 0 and infinity. Therefore the lifetime is considered as the average lifetime of the particles in the excited state:

$$<t> = \tau = \frac{\int_0^\infty t N_2(t) dt}{\int_0^\infty N_2(t) dt} \quad (2.32)$$

$$= \frac{\int_0^\infty N_0 t e^{-A_{21}t} dt}{\int_0^\infty N_0 e^{-A_{21}t} dt} \quad (2.33)$$

In the denominator the total number of particles are calculated for normalization, while in the numerator the time for each particle is calculated and integrated over the full time interval. The integration in the numerator can be done with partial integration (see chapter 10.2). With that we obtain as a solution:

$$\tau = \frac{\int_0^\infty t N_0 e^{-A_{21}t} dt}{\int_0^\infty N_0 e^{-A_{21}t} dt} = \frac{N_0}{A_{21}} \quad (2.34)$$

$$= \frac{N_0}{A_{21}} = \frac{1}{A_{21}} \quad (2.35)$$

This simple result states that the average lifetime is directly related to the Einstein coefficient $A_{21}$. The population of state 2 is reduced to $\frac{1}{e}$ of its initial value after $\frac{1}{A_{21}}$. Furthermore, based on the relation in equation 2.29, the Einstein coefficient $B$ can be calculated from the lifetime as well.

Another important parameter in spectroscopy is the linewidth. A high linewidth might obscure additional information and lead to low intensity. Nevertheless, linewidth also contains significant information on the material of study.

Mathematically, the (natural) linewidth is the root mean square deviation from the expectation value - in our case $\tau$. For the general definition of the standard
deviation see chapter 10.3. In our case, we have to calculate:

\[
(\Delta t)^2 = \frac{\int_0^\infty (t - \tau)^2 N_2(t) dt}{\int_0^\infty N_2(t) dt} = \tau^2
\]  

(2.36)

[The integral can be solved by double application of partial integration]

The natural linewidth is the minimum linewidth that originates from the variation of the lifetime of the excited state. Other factors influencing linewidth are given below.

A relation to the frequency of the natural linewidth can be obtained from the Heisenberg uncertainty principle

\[
\Delta E \ast \Delta t \geq \frac{\hbar}{2}
\]

(2.37)

with \( \hbar = \frac{h}{2\pi} \).

With the above relation for the standard deviation we obtain

\[
\Delta \nu \geq \frac{1}{4\pi \tau}
\]

(2.38)

The linewidth is experimentally obtained mainly by the full width at half maximum (FWHM) or half height (FWHH), \( \delta \nu_{\text{FWHM}} = \frac{1}{2\pi} \) which is exactly twice the linewidth.

Now that we derived the natural linewidth of spectroscopic lines, which sets the lower limit for the linewidth - all other influences will just increase it - we will briefly discuss further sources of linebroadening. Let’s first describe a characteristic of a line being named either ‘homogenous’ or ‘inhomogenous’. The differences are summarized in table 2.1:

An inhomogenously broadened line is in fact a superposition of many individual lines that can’t be resolved. See the experimental way to separate the two lines below. The mathematical functions for the Lorentzian and Gaussian line are as follows:

\[
L : f(\omega) = \frac{1}{1 + (\omega_0 - \omega)^2 T_d^2}
\]

(2.39)

\[
G : \phi(z) = \frac{1}{\sqrt{2\pi}} e^{-z^2}
\]

(2.40)
Table 2.1: Differentiation between homogenous and inhomogenous broadening.

<table>
<thead>
<tr>
<th>specification</th>
<th>homogenous</th>
<th>inhomogenous</th>
</tr>
</thead>
<tbody>
<tr>
<td>all particles</td>
<td>are alike</td>
<td>are not alike</td>
</tr>
<tr>
<td>transition probabilities</td>
<td>same</td>
<td>different</td>
</tr>
<tr>
<td>lineshape</td>
<td>mainly Lorentzian</td>
<td>mainly Gaussian</td>
</tr>
</tbody>
</table>

* see chapter 2.6

$T_d$ describes the time constant for the damping.

Linebroadening can occur because of the measurement device, motion or from the use of too high radiofrequency power. We will discuss three cases, Doppler broadening, pressure broadening, and saturation broadening.

1. Doppler broadening

The Doppler effect comes across everyday life frequently if an ambulance or police car passes by. One observes a frequency change due to relative motion of source and receiver of electromagnetic radiation. Mathematically this can be expressed as

$$\omega - \omega_0 = \vec{k}\vec{v}$$

(2.41)

where $\omega$ is the observed and $\omega_0$ the emitted frequency, $\vec{v}$ the velocity and $\vec{k} = \frac{\omega_0}{c_0}$ the wave vector.

Simplified in a 1D-variant,

$$\omega = \omega_0(1 + \frac{v_x}{c_0})$$

(2.42)

$$\Leftrightarrow v_x = c_0 \frac{\omega - \omega_0}{\omega_0}$$

(2.43)

This leads to an intensity distribution

$$I(\omega) = I(\omega_0)e^{-\frac{v_x^2}{2v_p^2}}$$

(2.44)

This represents a Gaussian function with $v_p = \sqrt{\frac{2kT}{m}}$ being the most probable velocity which is obtained from the velocity distribution using Maxwell-Boltzmann derivation.
2.4. LIFETIME AND LINEWIDTH

The corresponding half-width is then given as

\[ \delta_{\text{Doppler}} = \frac{\omega_0}{c_0} \sqrt{\frac{8kT \ln 2}{m}} \]  

(2.45)

2. Pressure broadening

Preferably in gases, pressure broadening can occur. Collisions between gas phase atoms or molecules occur with energy exchange which can lead to a shortening of the lifetime of an excited state and following also to linebroadening. The linewidth can simply be expressed as

\[ \frac{\delta_1}{2} = \frac{1}{2\pi \tau} \]  

(2.46)

with \( \tau \) being the mean time between collisions.

This will show the same lineshape behavior as the natural linewidth (Lorentzian).

To verify if pressure broadening occurs, the pressure should be lowered and a reduced linewidth indicates pressure broadening.

3. Saturation broadening

If a high-power source of electromagnetic radiation is used, the Boltzmann statistics of the population difference between two energy states can be severely influenced, up to the case that all particles are in the higher electronic state. This will increase the number of spontaneous emissions and therefore increase the linewidth. For a homogeneously broadened line the central intensity will therefore decrease and the intensity around the central point increase. In opposition to this an inhomogeneously broadened line will show a decreased intensity at the specific frequency and no influence on the other intensity since these are all individual lines. This phenomenon is also called 'hole burning' and can be used to differentiate homogenous and inhomogenous broadening, see Fig. 2.6.

Similar to pressure broadening, saturation broadening can be identified by recording spectra with different radiation power.
2.5 Interaction of Matter with Electromagnetic Radiation

As was demonstrated in chapter 2.1, electromagnetic radiation is composed of an electric and a magnetic field. Therefore, any kind of matter can interact with either of the two fields.

Interactions with the magnetic field are limited to components containing a magnetic moment (see below) such as nuclear spins (see chapter 4) or electron spins (see chapter 5) and atoms in principle where electron spin & orbit is coupled (RS-coupling or jj-coupling, see chapter 3.

The majority of interactions of matter deals with the electric field which we will focus on. A similar discussion can - in principle - also be done for magnetic field interactions.

In the following, we will give a general expression to describe the charge in a given molecule (here water). This illustrates terms we need later on and are commonly used. It is especially useful for large molecules with multiple atoms.

In general, the electric potential (or electrostatic potential) is described with the help of the charge density \( \rho(\vec{r}) \):

\[
\phi(\vec{R}) = \frac{1}{4\pi\varepsilon_0} \int_V \frac{\rho(\vec{r}) d\vec{r}}{|\vec{R} - \vec{r}|}
\]  

(2.47)
2.5. INTERACTION OF MATTER WITH ELECTROMAGNETIC RADIATION

If discrete charges are present as for the water molecule given in Fig. 2.7 the electric potential can be described as:

\[
\phi(R) = \frac{1}{4\pi\varepsilon_0} \sum_{n=1}^{N} \frac{q_n}{|R - r|}
\]  

(2.48)

(it is important that the point of observation is far away from the charges, \( R \gg r \))

Figure 2.7: Definition of the coordinates system for the water molecule.

The use of this equation is limited especially for large molecules with a high number of atoms. Therefore, a Taylor expansion (see chapter 10.1) with respect to powers of \( 1/R \) is performed. This shows that the potential of any charge distribution can be represented by a sum of multipoles:

\[
\Rightarrow \phi(R) \approx \phi^{(0)} + \phi^{(1)} + \phi^{(2)} + \cdots
\]  

(2.50)

Due to the power dependence the contribution to the electric potential decreases rapidly with increasing power. The first term \( \phi^{(0)} \) is the coulomb potential containing charges (monopole) and is therefore zero for neutral molecules. The second term is called the dipole moment which is in most cases the important one. It can be expressed as

\[
\phi^{(1)} = \frac{\vec{\mu} \cdot \vec{r}}{r^3} = \frac{\vec{\mu} \cdot \vec{e}_r}{r^2}
\]  

(2.51)
CHAPTER 2. ABSORPTION AND EMISSION OF RADIATION

with \( \epsilon_r \) being the unit vector in \( \vec{r} \) direction. \( \mu \) is then defined as

\[
\mu = \sum_{i=1}^{N} q_i r_i
\]  

(2.52)

The dipole moment indicates the charge distribution of a molecule (see below).

The third term is called the quadrupole moment and is a tensor which describes the deviation of charge distribution from spherical symmetry. The individual components of the tensor are:

\[
\theta_{ij} = \frac{1}{2} \sum_{n=1}^{N} q_n [3(x_n)_i(x_n)_j - r_n^2 \delta_{ij}]
\]  

(2.53)

\( \delta_{ij} \) is the Kronecker delta, being 1 if \( i = j \) and 0 if \( i \neq j \).

Higher terms can be defined but are of little use only.

For the dipole moment being a vector, it is usually expressed as an arrow originating at the negative (partial) charge towards the positive (partial) charge. For more complicated molecules one can first calculate the centers of gravity for the negative and positive charges individually and then draw the dipole moment vector. For a molecule such as CO\(_2\) the centers of gravities of negative and positive charge are the same which means that there is no net dipole moment!

Let’s take the CO\(_2\) molecule to calculate its quadrupole moment. It is a tensor represented by a 3x3 matrix for the three cartesian coordinates:

\[
\theta = \begin{pmatrix}
\theta_{xx} & \theta_{xy} & \theta_{xz} \\
\theta_{yx} & \theta_{yy} & \theta_{yz} \\
\theta_{zx} & \theta_{zy} & \theta_{zz}
\end{pmatrix}
\]  

(2.54)

The quadrupole moment is a traceless tensor meaning

\[
Tr\theta = \theta_{xx} + \theta_{yy} + \theta_{zz} = 0
\]  

(2.55)

If we put the origin of our cartesian coordinate in the center of gravity of the CO\(_2\) molecule (which is valid only if no charges and no dipole moment exists), we have a 1D orientation in the z-axis with the two oxygens at positions \( r \) and \(-r\) from the carbon in the origin and yielding same values for the x- and y-direction. With the definition in equation 2.53 the three trace components can be calculated:

\[
\theta_{zz} = \frac{1}{2} [-Q(3r^2 - r^2) + 2Q*0 - Q(3(-r)^2 - (-r)^2)] = -2Qr^2
\]  

(2.56)

\[
\theta_{xx} = \theta_{yy} = \frac{1}{2} [-Q(-r^2) + 2Q*0 - Q(-(r)^2)] = +Qr^2
\]  

(2.57)
Table 2.2: Dipole and quadrupole moments of selected molecules.

<table>
<thead>
<tr>
<th>molecule</th>
<th>$\mu \left[ * 10^{-30} C m \right]$</th>
<th>$\theta_{zz} \left[ * 4.487 \cdot 10^{-40} C m^2 \right]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>6.0</td>
<td>1.76</td>
</tr>
<tr>
<td>HCl</td>
<td>3.44</td>
<td></td>
</tr>
<tr>
<td>HBr</td>
<td>2.64</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0</td>
<td>-3.3</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>4.97</td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>0</td>
<td>-6.7</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>6.17</td>
<td></td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>5.71</td>
<td></td>
</tr>
<tr>
<td>KF</td>
<td>24.4</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>34.7</td>
<td></td>
</tr>
<tr>
<td>KBr</td>
<td>35.1</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td></td>
<td>56</td>
</tr>
</tbody>
</table>

As described above, we obtain a traceless tensor.

Table 2.2 give some examples of the dipole and quadrupole moment of some molecules.

A similar computation can be done for the magnetic potential which yields the magnetic moment (see chapter 4). A detailed calculation is omitted here.

Molecules that do not have a dipole moment such as CO$_2$ or CH$_4$ can nevertheless be measured with spectroscopic techniques. This is possible since an electric field can induce an electric dipole moment. This phenomenon is linked to the term polarizability. For a molecule with a permanent dipole moment a partial alignment in the direction of the electric field is possible, which is known as orientation polarization. This is a rather slow and temperature dependent process since the thermal motion of the molecules is opposed to the electric field.

For a molecule without dipole moment, the displacement polarization generates
an induced dipole moment due to displacement of nuclei in opposition to the electron shell or ions in a molecule or crystal lattice. The polarizability $\alpha$ is a tensor and the induced dipole moment can be expressed as

$$\mu_{\text{ind}} = \vec{\alpha} \ast \vec{E} + (\vec{\beta} \vec{E}^2 + \vec{\gamma} \vec{E}^3) \quad (2.58)$$

The linear relation is sufficient in most cases. Just for application in non-linear optics the other two terms become relevant.

### 2.6 Transition Probabilities

So far we have discussed the general properties and consequences of absorption and emission of electromagnetic radiation. Additionally, we have to think about transition probabilities, the question how probable a certain transition is. This, in principle, requires a quantum mechanical approach. We will only briefly touch this here.

First, let’s consider classically an electric dipole where the charge distribution changes with frequency. This can be described as

$$\vec{\mu}(t) = \vec{\mu} \cos \omega t \quad (2.59)$$

Classically, the average radiant power of such a spontaneous radiating dipole is defined as [4]

$$<P_{\text{em}}> = \frac{1}{4\pi \epsilon_0} \frac{2}{3c^3} <\left[ \frac{d^2 \vec{\mu}(t)}{dt^2} \right]^2> = \frac{\omega^4 \vec{\mu}^2}{12\pi \epsilon_0 c^5} \quad (2.60)$$

For the derivation we have used the fact that the time average of a $\cos^2$ function is equal to $\frac{1}{2}$.

For a transition to quantum mechanics the dipole moment vector is transferred to an operator description

$$\vec{\mu} \rightarrow \hat{\mu} = 2q \hat{\mathbf{r}}$$

The factor 2 comes into play because of the two states of the electron spin ($\pm \frac{1}{2}$) which has no analogue in classical representation.

By definition, the transition moment is generally defined for a transition from state 1 to state 2 as

$$M_{21} = \int \psi_2^* \hat{\mu} \psi_1 d\tau \quad (2.62)$$
The integration runs over all variables of the wave function (in this case space).

For the expectation value we then obtain in analogy to the classical case

\[
<P_{21} > = \frac{\omega^4}{3\pi\epsilon_0\epsilon_0'} |\vec{M}_{21}|^2 
\]

(2.63)

\(\vec{M}_{21}\) being a vector means that

\[|\vec{M}_{21}|^2 = M_{21,x}^2 + M_{21,y}^2 + M_{21,z}^2\]  

(2.64)

For the Einstein coefficient of the spontaneous emission we then obtain

\[A_{21} = \frac{< P_{21} >}{\hbar\nu} = \frac{16\pi^3\nu^3}{3\epsilon_0\epsilon_0'\hbar} |\vec{M}_{21}|^2\]  

(2.65)

With the relation between \(A_{21}\) and \(B_{21}\) (see equation 2.27) we get an expression for the latter

\[B_{21} = \frac{2\pi^3}{3\epsilon_0\hbar^2} |\vec{M}_{21}|^2\]  

(2.66)

Though the expression looks straightforward, transition moments and with that transition probabilities are rarely calculated. Nevertheless, as we will see in chapter 3, by using simple symmetry arguments it is possible to state if a transition moment is 0 and therefore forbidden or if it is different from 0 and therefore an allowed transition.

### 2.7 Fourier Transform

At the end of this chapter, we will briefly speak about the importance of Fourier transform in modern spectroscopy.

The basic idea of Fourier transform is based on the decomposition of any time dependent function \(s(t)\) into harmonic waves with variable frequency \(\omega\). The mathematical directive goes as

\[
g(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(\omega)e^{i\omega t} d\omega 
\]

(2.67)

\[f(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(t)e^{-i\omega t} dt\]  

(2.68)

Keep in mind that \(e^{i\omega t} = \cos \omega t + i \sin \omega t\) which is interpreted as the 'real' and 'imaginary' in many spectroscopies.
The important conclusion is that the same information content is present in frequency and time domain. Time and frequency are therefore also known as ‘Fourier pairs’. In practice, one can excite a spectrum as a whole and record the time response which then is transferred to a frequency distribution, which is more familiar to us. Clearly, a significant time gain is possible in this way instead of screening the frequency range.

The integration is often too time consuming to be done and therefore is usually transformed into a discrete Fourier transform with discrete time intervals that are used for digitization of the incoming time dependent signal:

\[
g(t) = \sum_{k=-\infty}^{\infty} c_k e^{i \frac{2\pi}{T} kt}
\]  

(2.69)

There exist some drawbacks of Fourier spectroscopy or at least points that one has to take care of. One obvious point is the digitization time. The digitization has to be fast enough so as to not obscure spectroscopic features (known as aliasing). The digitization time (also named dwell time) also sets the spectral width and therefore sets which frequency range can be sampled. The second point to be mentioned is the number of digitization points. If the number of points is too small so that not the full time signal is recorded, this results in so-called wiggles in the frequency domain, as can be seen in figure 2.8.

![Figure 2.8: Demonstration of the occurrence of wiggles in spectra in part a. Part b shows a correct truncation of the time domain signal.](image)
To illustrate the relationship between time and frequency signals, let’s consider a few examples shown in figure 2.9.

![Rectangular](image1)

![Sinc](image2)

![Gaussian](image3)

![Lorentzian](image4)

Figure 2.9: Examples of time domain and the corresponding frequency domain signals.

Finally, two further points should be addressed (see fig. 2.10). Signals in the frequency domain with different signals are reflected in the time domain by different oscillation frequencies. Linebroadening in the frequency domain refers to a decaying function in the time domain (Fig. 2.11). This can be understood since because of the inverse proportionality of frequency and time a short time domain signal refers to a broad frequency signal and vice versa a signal with a long time domain refers to a narrow signal. Secondly, different frequencies - also named frequency offsets - are visible in the time domain by oscillations.
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Figure 2.10: Illustration of frequency offset and its effect in the time domain.

Figure 2.11: Linebroadening in time and frequency domain.

2.8 Questions for Recapitulation

1. Calculate the corresponding wavelength for different temperatures: 300 K (room temperature), 2700 K (conventional light bulb), 3200 K (halogen lamp), 5800 K (sun light), and 7000 K (energy saving lamp) assuming they behave like a black body (color temperature). To which colors do they correspond?
2. Verify the result for the standard deviation of the average lifetime using partial integration!

3. Calculate the line broadening due to the Doppler effect for the different spectroscopic techniques assuming a moving source with a velocity of 5 mm s$^{-1}$ given the following values:
   - NMR: $\nu = 100$ MHz
   - ESR: $\nu = 4$ GHz
   - IR: $\lambda = 10$ $\mu$m
   - VIS: $\lambda = 500$ nm

2.9 References


general literature:
Chapter 3

Structure and Symmetry

3.1 Quantum Mechanics of the Hydrogen Atom

We will use the general results of quantum mechanics to finally come to a representation of the electron orbitals of the hydrogen atom.

Max Planck in 1900 postulated the relation between energy and frequency.

\[ E = n \hbar \nu \] (3.1)

In the form given here, \( n \) being an integer can be seen as referring to the 'shell' given by Bohr's atomic model. As we will see below it’s called the principal quantum number.

Different experiments gave evidence that particles, e.g., light photons, behave both as particles and as a wave. The latter is the prerequisite of electromagnetic radiation while the former is demonstrated, e.g., by the Compton effect. De Broglie assigned in 1924 all moving particles with momentum \( p \) a wavelength according to \( p = \frac{h}{\lambda} \). Later on, Max Born in 1926 formulated a solution to the particle-wave duality. Not the wave function \( \psi(x, y, z, t) \) itself but the product with its complex conjugate \( \psi \psi^* \) has the physical meaning of the probability to find a particle at position \((x, y, z)\) at a given time \(t\). The wave function is used in Schrödinger's equation

\[ \mathcal{H} \psi = E \psi \] (3.2)

Representing the Hamilton operator \( \mathcal{H} \) acting on the wave function yielding energy times the wavefunction. Functions fulfilling the equation are called eigenfunctions with the energy values called eigenvalues. The Hamilton operator denotes
a mathematical directive. As an example, for a particle of mass \( m \) moving along a potential \( \phi \) in x-direction we would write

\[
\mathcal{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \phi(x)
\]  

(3.3)

In three dimensions we get

\[
\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + \phi(x)
\]

(3.4)

with \( \nabla \) called the Nabla operator and \( \nabla^2 = \Delta \) named Laplace operator defined as

\[
\Delta = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}
\]

(3.5)

As we will see below, it is often advantageous to convert from Cartesian \((x, y, z)\) to spherical coordinates \((r, \theta, \phi)\). The relations are given in Chapter 10.4. The Laplace operator then reads as

\[
\Delta = \nabla^2 = \frac{1}{r^2 \sin \theta} \left[ \sin \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \phi^2} \right]
\]

(3.6)

For completeness, the time-dependent Schrödinger equation can be written as

\[
\mathcal{H} \psi = i\hbar \frac{\partial \psi}{\partial t}
\]

(3.7)

With this general description, we can now describe the situation in the hydrogen atom with an electron of charge \(-e\) moving in the electric field of a nucleus with charge \(e\). The potential is then simply the Coulomb potential of a point charge and the Hamiltonian can be written as

\[
\mathcal{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}
\]

(3.8)

\(m_e\) is the reduced mass of the electron.

In the hydrogen atom, representation with spherical coordinates is obviously superior to Cartesian coordinates. In principle, there are different solutions to the Schrödinger equation possible, but one clever way is to represent the wave function
as a product of functions that only depend on one variable and are well-known functions.

\[ \psi(r, \theta, \phi) = R_{nl}(r)N_{|m|}R_{m}\,e^{im\phi} = R_{nl}(r)Y_{lm}(\theta, \phi) \quad (3.9) \]

The indices represent the quantum numbers being all integer with the following definition

- \( n \) - principal quantum number
- \( l \) - orbital quantum number with \( l < n \)
- \( m \) (also \( m_l \)) - magnetic (or orientational) quantum number with \(-l \leq m \leq l\)

Be aware that the functionalization of the wave function (right side of equation 3.9) results in functions that only depend on two quantum numbers.

The radial wave function \( R_{nl}(r) \) is often expressed with respect to the Bohr radius \( a_0 \) to get the dimensionless quantity \( \rho = \frac{r}{a_0} \). The expressions for \( R \) are given as

\[
R_{10} = \frac{1}{\sqrt{a_0^3}} 2e^{-\rho} \quad (3.10)
\]
\[
R_{20} = \frac{1}{\sqrt{8a_0^3}} (2 - \rho)e^{-\frac{\rho}{2}} \quad (3.11)
\]
\[
R_{21} = \frac{1}{\sqrt{24a_0^3}} \rho e^{-\frac{\rho}{2}} \quad (3.12)
\]
\[
R_{30} = \frac{1}{\sqrt{243a_0^3}} (6 - 6\rho + \rho^2)e^{-\frac{\rho}{2}} \quad (3.13)
\]
\[
R_{31} = \frac{1}{\sqrt{486a_0^3}} (4 - \rho)\rho e^{-\frac{\rho}{2}} \quad (3.14)
\]
\[
R_{32} = \frac{1}{\sqrt{2430a_0^3}} \rho^2 e^{-\frac{\rho}{2}} \quad (3.15)
\]

Graphical representations of \( R \) as a function of distance \( r \) are given in Fig. 3.1 together with the radial density function \( 4\pi^2r^2R_{nl}^2 \) which represents the probability of finding an electron in the radial direction.
The function $N_{|l|m}$ is simply a normalization factor. $P_{|l|}^{m}(\theta)$ are called associated Legendre polynomials, the definitions are given in chapter 10.5. The angular dependence on both $\theta$ and $\phi$ are summarized in the spherical Laplace function $Y_{lm}(\theta, \phi) = N_{|l|m} P_{|l|}^{m}(\cos \theta)e^{im\phi}$. The definitions up to $l = 2$ are given below. They are both represented as spherical and Cartesian coordinates with the use of the relation $e^{ix} = \cos x + i \sin x$.

\[
Y_{00} = \frac{1}{\sqrt{4\pi}} \tag{3.17}
\]
\[
Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \tag{3.18}
\]
\[
Y_{1\pm1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi} = \mp \sqrt{\frac{3}{8\pi}} \frac{x \pm iy}{r} \tag{3.19}
\]
3.1. QUANTUM MECHANICS OF THE HYDROGEN ATOM

\[ Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) = \sqrt{\frac{5}{16\pi}} \frac{3z^2 - r^2}{r^2} \quad (3.20) \]

\[ Y_{2\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi} = \mp \sqrt{\frac{15}{8\pi}} \frac{(x \pm iy) z}{r^2} \quad (3.21) \]

\[ Y_{2\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi} = \sqrt{\frac{15}{32\pi}} \frac{(x \pm iy)^2}{r^2} \quad (3.22) \]

Now we want to express a spatial representation of the wave functions. For that the complex functions are a problem. But one result of quantum mechanics is that for functions with the same energy eigenvalue \((Y_{lm})\) are \(l\)-fold degenerate) a linear combination of degenerate functions are also solutions to the Schrödinger equation. Therefore subtraction and/or addition of two functions will eliminate the imaginary or real component. An example is to be calculated in the questions of recapitulation. In a short notation the wave functions get indices consisting of the principal quantum number \(n\), a small letter for the orbital quantum number \(l\) being \(s, p, d, f, g, h, \ldots\) for \(l = 0, 1, 2, 3, 4, 5, \ldots\) and the coordinates the wave function depends on. For \(l = 0\) we get only one wave function, for \(l = 1\) there are three for the three coordinates \(x, y, \text{and } z\). For \(l = 2\) we obtain five and for \(l = 3\) seven wave functions. Up to \(n = 3\) the wave functions are given as

\[ \psi_{1s} = \sqrt{\frac{1}{4\pi}} R_{10} \quad (3.23) \]

\[ \psi_{2p_x} = \sqrt{\frac{3}{4\pi}} R_{21} \frac{x}{r} \quad (3.24) \]

\[ \psi_{2p_y} = \sqrt{\frac{3}{4\pi}} R_{21} \frac{y}{r} \quad (3.25) \]

\[ \psi_{2p_z} = \sqrt{\frac{3}{4\pi}} R_{21} \frac{z}{r} \quad (3.26) \]

\[ \psi_{3d_{z^2}} = \sqrt{\frac{5}{4\pi}} R_{30} \frac{3z^2 - r^2}{2r^2} \quad (3.27) \]

\[ \psi_{3d_{xz}} = \sqrt{\frac{15}{4\pi}} R_{31} \frac{xz}{r^2} \quad (3.28) \]

\[ \psi_{3d_{yz}} = \sqrt{\frac{15}{4\pi}} R_{31} \frac{yz}{r^2} \quad (3.29) \]

\[ \psi_{3d_{x^2-y^2}} = \sqrt{\frac{15}{4\pi}} R_{32} \frac{x^2 - y^2}{2r^2} \quad (3.30) \]
With these descriptions of the wavefunctions we can generate a 3-dimensional representation of the so-called electron orbitals. While for the spherical s-orbitals this can be easily done including the representation of nodes changing the sign of the wave function with different colors (see Fig. 3.2), this becomes nearly impossible for p- and d-orbitals.

\[
\psi_{3d_{xy}} = \sqrt{\frac{5}{4\pi}} R_{32} \frac{xy}{r^2}
\]  

(3.31)

A more simple way is to present the wavefunctions by drawing orbitals representing a 90% probability that the electron is inside this area. In this way 2p and 3d orbitals can be represented as shown in Fig. 3.3. Two-dimensional representations are also possible in this way. A change in sign of the wavefunction is indicated by + and - or shades in different color. One has to keep in mind though that there is a 10% probability that the electron is outside the given space of the orbital.
3.2 Molecular Orbitals

We consider the simplest molecule which is the hydrogen molecular ion $H_2^+$ since it contains only one electron together with two nuclei. A full quantum-mechanical treatment is only possible by the use of the Born-Oppenheimer approximation. This tells us that the electron being so much lighter than the nuclei it will move considerably faster than the nuclei which means that the internuclear distance $R$ can be fixed (for the ground state of a molecule this is clearly valid; one can assume that in a given time a nucleus moves by 1 pm while at the same time the electron moves $1000$ pm). With this approximation we can define the Hamilton operator for the electron in the electric potential of two nuclei $A$ and $B$:

$$\mathcal{H} = \frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{r_A} + \frac{1}{r_B} \right)$$ \hspace{1cm} (3.32)

For the full description of the system, the nuclear repulsion has to be included

$$\Phi_{\text{repulsive}} = -\frac{e^2}{4\pi\varepsilon_0 R}$$ \hspace{1cm} (3.33)

The Schrödinger equation can be exactly calculated and for a given value $R$ the
energy eigenvalues are obtained. Combining these we obtain the potential curve in this system as exemplified in Fig. 3.4.

Figure 3.4: Potential curve of diatomic molecules. $D_e$ denotes the dissociation energy and $r_e$ the equilibrium distance.

Any further molecule is not anymore exactly calculable. Therefore we will adapt a scheme that is rather simple and good for qualitative results. Let’s assume in the $H_2^+$ molecule that the electron is near nucleus A. Then we can disregard the potential from nucleus B since $r_A \ll r_B$ or $\frac{1}{r_A} \gg \frac{1}{r_B}$. The opposite is true if the electron is near nucleus B. Therefore we can describe the resulting wave function as a combination of two atomic orbitals

\[
\psi = N[\psi_{1s}(A) + \psi_{1s}(B)] \tag{3.34}
\]

\[
\psi^2 = N^2[\psi_{1s}^2(A) + \psi_{1s}^2(B) + 2\psi_{1s}(A)\psi_{1s}(B)] \tag{3.35}
\]

$N$ is the normalization factor to ensure that $\int \psi^2 d\tau = 1$. The term

\[
S = \int \psi_{1s}(A)\psi_{1s}(B)d\tau \tag{3.36}
\]

is called the overlap integral and indicates an increased electron density between the two nuclei.
3.2. Molecular Orbitals

The methodology we applied here is known as Linear Combination of Atomic Orbitals or LCAO method (sometimes named as LCAO-MO, the latter for Molecular Orbital). The resulting function is called a bonding orbital and in this case due to the rotational symmetry about the internuclear axis it is called a $\sigma$ orbital (see Fig. 3.5).

In a similar way the subtraction of the two atomic orbitals results in an antibonding orbital:

$$\psi = N[\psi_{1s}(A) - \psi_{1s}(B)] \quad (3.37)$$

$$\psi^2 = N^2[\psi_{1s}^2(A) + \psi_{1s}^2(B) - 2\psi_{1s}(A)\psi_{1s}(B)] \quad (3.38)$$

The last term reduces the electron density between the nuclei. The antibonding orbital is indicated by an asterisk, in this case a $\sigma^*$ orbital.

In a similar manner we can create molecular orbitals from other atomic orbitals. For the three p-orbitals two different types of molecular orbitals are created. By definition the z-direction points along the internuclear vector. A combination of two $p_z$ orbitals therefore also yields a $\sigma$ orbital while combination of two $p_x$ or two $p_y$ orbitals will generate $\pi$ orbitals with a node through the internuclear axis. The graphical representation is also included in Fig. 3.5. Clearly, a combination of a $p_x$ and a $p_y$ orbital cannot generate a bonding orbital.

Depending on the energy values of the individual atomic orbitals also other combination of orbitals are possible, e. g., combination of an $s$ and a $p_z$ orbital or of a $p_x$ and a $d_{xy}$ orbital. With $d$ atomic orbitals we can also generate $\delta$ molecular orbitals. Finally, there can be also non-bonding orbitals existing though they have no influence on the total energy of the molecule.

![Figure 3.5: Bonding and antibonding molecular orbitals of $H_2^+$.](image)

In a traditional MO scheme the molecular orbitals are filled from bottom to
Another practical rule is that $N$ atomic orbitals will create $N$ molecular orbitals. With that it can clearly be seen that the $H_2$ molecule is energetically more stable than two individual hydrogen atoms (Fig. 3.6). Consequently, a molecule such as $\text{He}_2$ will not exist (an antibonding orbital is always slightly more antibonding than a bonding orbital bonding). Nevertheless, a $\text{He}_2^+$ molecule should be able to exist and was also experimentally observed.

Finally, consider the different MO schemes of $N_2$ and $O_2$ (Fig. 3.7).
For \( \text{O}_2 \) the procedure is straightforward with the restriction that degenerate orbitals \( (2\pi^*) \) are first filled with one electron only. This way it is easy to demonstrate why the oxygen molecule is paramagnetic. The situation is different for the nitrogen molecule. The order of the orbitals is reversed between \( 2p\pi \) and \( 2p\sigma \) orbitals. This is because we have to take into account overlap of \( 2s \) and \( 2p \) orbitals. This is more relevant for lighter atoms because of smaller shielding effects (see chapter 3.3). The energy separation between \( 2s \) and \( 2p \) orbitals increases along the period. Therefore, for nitrogen (and lighter possible molecules in the 2\textsuperscript{nd} period) we have to consider a more complex LCAO wave function:

\[
\psi = c_2s\psi_2s(A) + c_{2p_z}\psi_{2p_z}(A) + c_2s\psi_2s(B) + c_{2p_z}\psi_{2p_z}(B) \tag{3.39}
\]

This is indicated in the MO diagram by dotted lines. The resulting \( 2s\sigma^* \) and \( 2p\sigma \) orbitals spread apart from each other (because of symmetry reasons) and therefore the \( 2p\pi \) orbital is the energetically lowest \( 2p \) MO.

### 3.3 Multi-Electron Systems, Term Symbol

For the systems we discussed in the previous chapters, a limited number of electrons were present that enabled a general description of the energy levels. We will now develop a more generalized way to define the energy ground state without the exact quantum mechanic description.

Similar to the classical energy values for the hydrogen atom this can be simply transferred to the quantum mechanic result

\[
E_{nlm} = -\frac{hc_0R_H}{n^2} \tag{3.40}
\]

The energy values - to first order - only depend on the principal quantum number \( n \). The quantum numbers are related by the inequality

\[
|m| \leq l \leq n - 1 \tag{3.41}
\]

For transitions between the different energy levels the following selection rules apply:

\[
\Delta l = \pm 1 \tag{3.42}
\]

\[
\Delta m = 0, \pm 1 \tag{3.43}
\]
There are no restrictions for changes to the principal quantum number \( n \).

The first rule can simply be explained from the conservation of angular momentum by taking into account that a photon has spin 1; this means that emission or absorption - meaning creation or destruction of a photon - changes the orbital quantum number by one.

The selection rules can be used to describe the spectral transitions in an alkali atom - this case sodium (Fig. 3.8). In a simplified picture we only consider the outermost single electron which is often named valence electron. The inner electrons are taken into account by their shielding effect since they shield the valence electron from the electric field of the nucleus. It is easy to see that for electrons in an \( s \)-orbital that according to the radial wave function have a non-zero charge density at the position of the nucleus (see chapter 3.1) the shielding is ineffective. Furthermore, for electrons in \( p \)- and \( d \)-orbitals the most probable position of charge move further away from the nucleus. Therefore the shielding effect of inner electrons is more effective for those. Combining these considerations one can correct the energies of the different transitions, however we will just mention the qualitative effects.

![Figure 3.8: Energetic transitions for the sodium atom.](image)

Historically, for the different values of the orbital quantum number \( l \) the letters \( s \), \( p \), \( d \), \( f \) for \( l = 0 \), 1, 2, 3 are used which are abbreviations of \textit{sharp}, \textit{principal}, \textit{diffuse}, and \textit{fundamental}. For larger values of \( l \) these are given the characters in alphabetical
order $g, h, i, k, \ldots$. For multi-electron systems, the orbital quantum numbers $l$ of the individual electrons is combined to a total orbital quantum number $L$. Therefore the states are labeled $S, P, D, F, \ldots$ in the same way as for single electrons.

The fourth quantum number is dedicated to the spin of the electron which is related to an intrinsic angular momentum (also nuclei can have spin). Stern and Gerlach showed in 1922 this phenomenon in their experiment. They used a beam of silver atoms (having a single $5s$ electron) to lead through an inhomogeneous magnetic field. The force acting on the electron ($\vec{\mu} \times \vec{B}$) lead to the occurrence of two spots of silver instead of a continuum like expected classically. Later this was given the expression of spin with values for a single electron of $s = \pm \frac{1}{2}$. For multi-electron system the individual spins are combined to a total spin $S$. Orbital angular momentum and spin combine to the total angular momentum

$$\vec{j} = \vec{l} + \vec{s}$$

(3.44)

From the selection rule $\Delta j = 0, \pm 1$ it follows that spin and orbital angular momentum can only be parallel and antiparallel in orientation. For the principal branch for the sodium atom (see above), we therefore obtain practically a doublet for the sodium-D line because of the possible transitions between the S-state with $j = \frac{1}{2}$ and the P-state with $j = \frac{5}{2}$ or $j = \frac{3}{2}$.

To characterize multi-electron systems with all the spin, orbital, and total angular momentum, the term symbol was created. The central point is the total orbital quantum number expressed by the symbols $S, P, D, F, \ldots$. On the top left of this the spin multiplicity is given according to $2S + 1$ to yield integer number. On the lower right the total angular momentum is given, see the derivation below. With this, one can characterize a multi-electron system with one simple expression. For the sodium D-line example, we would have transitions between a $^2 \! S_{\frac{1}{2}}$ and $^2 \! P_{\frac{3}{2}}$ or $^2 \! P_{\frac{1}{2}}$ states.

For multi-electron systems, a few rules exist how the electrons are distributed on the different orbitals. The first rule applies to all orbitals and is called the Pauli-principle after Wolfgang Pauli. In general it states, that two electrons cannot have four identical quantum numbers. More applied it means that in an orbital (which can fit maximum two electrons) with two electrons they have to have opposite spin.

Additionally, there are rules named after Friedrich Hund (practically there are four rules, the first being that fully occupied shells with quantum number $n$ have
a total angular momentum $j = 0$). One is that the term with maximum $S$ has the lowest energy and the other one that for the given $S$ the one with the largest $L$ has lowest energy:

$$ S = \text{Max} \left( \sum_i m_i^S \right) \quad (3.45) $$

$$ L = \text{Max} \left( \sum_i m_i^L \right) \quad (3.46) $$

The maximum number for $S$ is easily obtained by first filling all orbitals with one electron in parallel orientation before adding a second electron with antiparallel spin into an orbital. For maximum $L$ consider that for a given $n$ and $l$, $m_l$ runs from $-l$ to $+l$. Then by first filling the electrons in the orbitals with larger $m_l$ the value for $L$ can be maximized. Nevertheless, it has to be kept in mind that first the maximum value of $S$ has to be obtained before maximizing $L$.

Finally, the total angular momentum can principally obtain values between $J = |L - S| \ldots L + S$. The ground state or lowest energy has the one with $J = |L - S|$ if the shells are less than half full and $J = L + S$ for shells that are more than half full (for half full shells $J = S$). The reason behind this can be explained in a way that spin and orbital angular momentum want to be antiparallel to each other (orbiting negative electron charge creates a magnetic field) which explains the value for less than half full shells. In the other case the missing necessary electron to fill the shell completely can be understood as 'holes' that creating an opposite magnetic field and therefore a parallel arrangement of $L$ and $S$ is energetically favored.

Remember that these rules apply to find the energetic ground state of a multi-electron system. All other combinations are possible, just require higher energy. In the ‘Questions of Recapitulation’ there are a few examples given to determine the energetic ground state of certain atoms. If there is more than one unoccupied shell, the value for $J$ is determined by the relation of the total number of electron to the total number of available electrons. Based on the term symbol the top left number for $2S + 1$ is referred to a singlet, doublet, triplet, quartet, ... energetic state for values of 1, 2, 3, 4, ...
Spin-Orbit Interaction

So far, we neglected interaction of the spin momentum and angular orbital momentum of an electron. Though if one takes into account coulomb interaction and magnetic interaction of electrons, it becomes clear that such an interaction can be significant.

Remember that a moving charge generates a magnetic field (just as in classical electrodynamics). Then an electron with spin angular momentum has a magnetic moment (spin) as well as the circulating current generated by the electron in an orbital surrounding the nucleus has a magnetic moment (orbital momentum). The interaction between these two magnetic moments is called spin-orbit interaction. The combination of the two will create a total angular momentum as the vector sum of the two momenta (further details will be given in chapter 5).

As can be easily understood, the spin-orbit coupling depends on the nuclear charge, the higher the charge the larger the current and therefore the larger the spin-orbit coupling (the spin magnetic moment interacts with the orbital magnetic field). In practice, the interaction scales with $\propto Z^4$ (Z: atomic number). For example, for a given system, for the hydrogen atom the coupling is $0.4 \text{ cm}^{-1}$, whereas for lead it is on the order of $1000 \text{ cm}^{-1}$!

With this information, two general scenarios have to be differentiated: In case of small spin-orbit interaction (mainly for light atoms), we speak of LS- or Russell-Saunders-coupling. Here, the spin momenta $s_i$ of the different electrons combine to a total spin $S$ as well as the individual orbital momenta $l_i$ to a total angular momentum $L$. $L$ and $S$ then are used to calculate the total angular momentum $J$. On the other hand for large spin-orbit interaction (mainly for heavy atoms), spin and orbital momentum of each electron combine to a total angular momentum $j = l + s$ which then are used to calculate the total angular momentum $J = \sum j_i$. This type is therefore called jj-coupling. The term symbol defined above is in principle for LS-coupling, though it often can still be used even for heavy atoms.

In a similar way to the term symbol for atoms one can define a symbol for molecules. Nevertheless it can become complicated to define this term symbol for arbitrary molecules. Therefore we will introduce the molecular term symbol for linear molecules where the internuclear axis is significant for space quantization.
It has the general form:

\[ 2S + 1 \Lambda^{(+/-)}_{\Omega,(g/u)} \]  

(3.47)

with the notations

- \( S \) is the total spin quantum number, identical to the atomic term symbol
- \( \Lambda \) is the similar expression related to \( L \) for the atom expressed with greek letters (\( \Sigma, \Pi, \Delta, \Phi, \ldots \)). A new quantum number \( \lambda = |m_l| \) is defined for a given molecular orbital. With that, \( \Lambda = |M_l| = |\sum m_{l,i}| \). Keep in mind, that due to the degeneracy for a linear molecule (\( \lambda \) and \( \Lambda \) defined from the absolute values), there are twice as many degenerate states if \( \Lambda \neq 0 \).
- \( \Omega \) is related to the total angular momentum of the molecule, \( \Omega = \Lambda + \Sigma \)
- \( u/g \) is defined with respect to the presence of an inversion point. If the wave function is unchanged due to a center of inversion, it is name \( g \) (from the german 'gerade', meaning even). If the wave function is changed it is named \( u \) (german 'ungerade', odd).
- \(+/-\) is defined with respect to the presence of an arbitrary mirror plane containing the internuclear axis, similar to \( u/g \), + meaning symmetry, - antisymmetric to the plane of reflection.

The definitions of \( u/g \) and \(+/-\) already lead to the next chapter dealing with the symmetry of molecular and orbitals. Beforehand, we shall illustrate the molecular term symbol by two examples:

The hydrogen molecule \( H_2 \) is characterized by two electrons with opposite spin, therefore \( S=0 \), a singlet state. \( \Lambda = 0 \) which results in a \( \Sigma \) term and \( \Omega \) therefore is 0 as well. The molecular term symbol therefore is

\[ ^1\Sigma_0 \]  

(3.48)

The ground state of the oxygen molecule \( O_2 \) was shown in Fig. 3.7. For the 1s and 2s electron shells being complete these can be disregarded. Then we are left with 2 electrons in the \( 2p\sigma \), 4 electrons in the \( 2p\pi \), and 2 electrons in the \( 2p\pi^* \) orbitals (remember the two latter electrons being both with parallel spin in two different
3.4. GROUP THEORY

orbitals). Then we get \( 2S + 1 = 3 \) and \( \Lambda = 0 \). By looking at the orbital symmetry, the \( 2p\pi^* \) orbital is a \( g \) term and we obtain for the molecular term symbol

\[
\Sigma_{g}^{-}
\]

The - comes from the antisymmetric behavior of the molecular orbital with respect to a mirror plane including the internuclear axis.

Using the molecular term symbol, the following selection rules for electronic transitions apply:

\[
\begin{align*}
\Delta \Lambda &= 0, \pm 1 \\
\Delta S &= 0, \\
\Delta \Omega &= 0, \pm 1 \\
\Sigma^+ &\leftrightarrow \Sigma^+ , \quad \Sigma^- &\leftrightarrow \Sigma^-
\end{align*}
\]

The total spin quantum number is retained, as long as there is no (significant) spin-orbit coupling.

3.4 Group Theory

While the quantum mechanical treatment of transitions is a correct way to determine transition dipole moments and with that transition probabilities, a consideration of symmetry arguments done in this chapter will at least determine if a transition is allowed or forbidden and therefore yield qualitative results. Additionally, this procedure is much simpler.

**Point Groups**

The symmetry of molecules, orbitals or three-dimensional objects in general can be described by certain symmetry operations that retain the original structure. For a molecule, this could mean that certain atoms cannot be differentiated due to symmetry reasons, e. g., in chloromethane (CHCl\(_3\)) a rotation by 120° around the C-Cl axis interchanges the different hydrogens.

Five different symmetry operations can be differentiated
• $C_n$: rotation through an angle $2\pi/n$

• $\sigma$: mirror plane

• $S_n$: combined rotation and mirror plane

• $i$: inversion center

• $E$: neutral element

Rotations have been explained above, the axis with the highest value of $n$ is called the principal axis of symmetry. Three different types of mirror planes can be defined. A horizontal mirror plane $\sigma_h$ is perpendicular to the principal axis of symmetry, while in a vertical one $\sigma_v$ the principal axis of symmetry lies in the mirror plane. Finally, a dihedral plane $\sigma_d$ halves the angle between two $C_2$ axes. Examples will be given below.

For the methane molecule the combination of a rotation through a $C_4$ axis and a horizontal mirror plane will resemble the original molecule, while the two alone would not do this. This is therefore called an $S_4$ symmetry. An inversion ($i$) through the center of the molecule can be envisioned in the ethane molecule where the two methyl groups are in a staggered conformation. The neutral element $E$ is existing for every molecule where no symmetry operations are done to the molecule.

All symmetry elements for a given molecule combined are called point groups. We will use the Schönflies notation which is more useful for molecules than the international Hermann Mauguin notation better suited for crystals. For example, a $C_{2v}$ symbol in the Schönflies notation corresponds to a $2mm$ in the Hermann Mauguin notation.

**Symmetry Group**

Further on, we will use the special properties of a symmetry group to derive certain characteristics of transition dipole moments. A symmetry group is set up by the following terms:

• a **symmetry group** contains all symmetry elements valid for a given molecule
the number of elements in a symmetry group determines its order. For example, if more than one \(C_2\) group exists, this is only counted once for the order.

derived from matrix considerations of symmetry operations, the character is a number relating to the symmetry of an operation, being +1 for symmetric, -1 for antisymmetric, and 0, ±2 if it is degenerate. They derive from irreducible matrix representations which will not be discussed here.

the symmetry type is used to denote certain symmetry principles. These are

- A, B: symmetric or antisymmetric with respect to \(C_{n, \text{max}}\)
- E, T: two- or threefold degeneracy
- 1, 2: symmetric or antisymmetric with respect to \(\sigma_v\)
- g, u: symmetric or antisymmetric with respect to \(i\)

To give more meaning to these definitions, consider the character table of the point group \(C_{2v}\) (Table 3.1), suitable for molecules such as \(\text{H}_2\text{O}\) or \(\text{SO}_2\).

Character tables are always symmetric, i. e., for a given number of symmetry elements the number of symmetry types has to be the same. The respective characters can be comprehended according to the symmetry types and the symmetry elements. For example, for symmetry type \(A_2\), the character for \(C_2\) has to be +1, while for \(\sigma(xz)_v\) it is -1. For this, the molecule is oriented in a way that the \(z\)-axis is in parallel to the \(C_2\) axis and the molecule lies in the \(xz\)-plane.
CHAPTER 3. STRUCTURE AND SYMMETRY

Some general considerations about character tables: The symmetry type \( A_1 \) or \( A_g \) contains for every symmetry element the character +1. All symmetry types have to be orthogonal to each other, i.e., multiplying the characters for a given symmetry element and adding them together has to yield 0. The last two columns in the character table contain geometric contributions. In the second to last column elements for translation and rotation are given. The assignments can also be followed by checking the corresponding characters for given symmetry elements. For the notations \( x \), \( y \), and \( z \) one can also consider the geometry of the p-orbitals. This column will later on be used to derive symmetry types that interact with the dipole moment (see below). The last column will be used for interactions with the polarizability tensor (see below). As a hint, relation to the symmetry of d-orbitals help for assignment to symmetry types. Orbitals reflecting the symmetry operations of a given symmetry type are then labeled accordingly with small letters, e.g., a \( p_x \)-orbital in the \( C_{2v} \) group would be named a \( b_1 \) orbital and so on.

There are numerous applications for character tables. Since we are interested in the absorption and emission of electromagnetic radiation, we have to consider the transition dipole moment (see chapter 2.6).

\[
\vec{M}_{21} = q \int \psi_2^* \vec{r} \psi_1 d\tau
\]  

(3.55)

with \( \vec{\mu} = q \vec{r} \) being the dipole moment. Application of group theory cannot calculate the transition dipole moment, but can give information if the integral is zero or non-zero. In the first case, the transition would be forbidden, otherwise allowed. For most cases, this information is sufficient.

Allowed transitions are from those symmetry types were all characters are +1 (\( A_1 \), \( A_g \), \( A_1g \)). For electronic transitions, with the help of the character table we have to multiply the symmetry types of the orbitals before and after transition with the corresponding mode of \( \vec{r} \), being \( x \), \( y \) or \( z \).

\[
X(x_1, x_2, x_3) \ast Y(y_1, y_2, y_3) \ast Z(z_1, z_2, z_3) = (x_1y_1z_1, x_2y_2z_2, x_3y_3z_3)
\]  

(3.56)

For the water molecule, a transition from an orbital \( a_1 \) to \( b_1 \) would be allowed if the corresponding symmetry type for \( \vec{r} \) would be of the type \( B_1 \), which is fulfilled for \( x \)-translation.
For electronic transitions the following arguments can be obtained:

- the symmetry type of the total state is derived from the product of the symmetry types of the individual electrons
- the symmetry type of an electron is identical to the symmetry type of the corresponding orbital
- only non-filled orbitals need to be considered

If the polarization tensor determines a possible transition (e.g., for Raman-interactions), the dipole moment has to be replaced by the polarization tensor containing mixed products $x_i x_j$ (see chapter 2.5). The corresponding tensor elements can be ordered according to $x^2, y^2, z^2, xy, xz, yz$, as is mentioned in the last column of the character table. These will be used further on to differentiate between IR-active and Raman-active vibrations of a molecule where a change to the dipole moment (IR) or the polarizability (Raman) is necessary.

To consider vibrations from multi-atomic molecules (diatomic molecules can only have one vibration), we have $3N-6$ possible vibrations with $N$ being the number of atoms. For linear molecules this reduces to $3N-5$ since rotations around the internuclear axis are not excited at normal temperatures due to the infinitely small angular momentum (compare to classical mechanics). For CO$_2$ we therefore would have four vibrations that are illustrated in Fig. 3.9 together with the calculations of the changes to the coordinates due to vibrations (internuclear axis is the $z$-axis, $y$-axis points upwards).

The four vibrations are named symmetric, antisymmetric and two bending vibrations. The factor $c$ for the positional change of the carbon atom can be determined from the masses of oxygen and carbon since the center of mass does not change during a vibration

$$2\beta m_O - c\beta m_c = 0 \iff c = 2 \cdot \frac{16}{12} = \frac{8}{3} \quad (3.57)$$

From these considerations, the symmetric vibration has the normal coordinate $\alpha$ and the asymmetric the normal coordinate $\beta$. The two bending vibrations with normal coordinates $\gamma$ and $\theta$ are degenerate and therefore have the same angular frequency.
CHAPTER 3. STRUCTURE AND SYMMETRY

Figure 3.9: Possible vibrations for CO$_2$ together with the coordinates of the individual atoms labeled 1-3 according to their structure being O, C, O.

With the character table the corresponding integrals for IR ($\int \psi_2^* x_i \psi_1 d\tau$) and Raman transitions ($\int \psi_2^* x_i x_j \psi_1 d\tau$) can be evaluated in accordance to the considerations given above for electronic transitions. If the resulting symmetry type is $A_1, A_g, A_{1g}$, the vibration is IR- or Raman active. A simplified rule states then that for an IR-active vibration

$$\frac{dp}{dq} \neq 0$$ (3.58)

and for Raman-active vibrations

$$\frac{dx}{dq} \neq 0$$ (3.59)

with $q$ being the normal coordinate. In the character table, the dimension of the vibrational subspace has to be calculated. It’s definition is as follows:

$$\text{Dim}U_i = \frac{h_i}{h} \sum_k h_k \text{Tr}(k) \chi_{i,k}$$ (3.60)

The definitions of the symbols are

- $\chi_{i,k}$: value of the character table (i-th representation, k-th class)
- $h_i$: dimension of i-th representation (for A, B 1, for E 2, and for T 3)
- $h_k$: order of the k-th class
- $h = \sum_k h_k$: order of the group

$\text{Tr}(k)$ is most easily calculated from

$$\text{Tr}(k) = n(k) * \alpha(k)$$ (3.61)
3.4. GROUP THEORY

<table>
<thead>
<tr>
<th>$k$</th>
<th>E</th>
<th>$\sigma$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
<th>$C_6$</th>
<th>$i$</th>
<th>$S_3$</th>
<th>$S_4$</th>
<th>$S_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha(k)$</td>
<td>3</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>-3</td>
<td>-2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.2: Values for $\alpha(k)$

Table 3.3: The character table for the group $C_{2h}$.

<table>
<thead>
<tr>
<th>$C_{2h}, 2/m$</th>
<th>E</th>
<th>$C_2$</th>
<th>i</th>
<th>$\sigma_h$</th>
<th>DimU</th>
<th>proper vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$R_z$</td>
<td>$x^2$, $y^2$, $z^2$, $xy$</td>
<td>6</td>
</tr>
<tr>
<td>$B_g$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>$R_x, R_y$</td>
<td>$xz$, $yz$</td>
<td>3</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$z$</td>
<td>3</td>
</tr>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$x, y$</td>
<td>6</td>
</tr>
<tr>
<td>trace</td>
<td>18</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>$\sum = 18$</td>
<td>$\sum = 12$</td>
</tr>
</tbody>
</table>

with $n(k)$ being the number of atoms that retain their position after a symmetry operation and $\alpha(k)$ obtained from Table 3.2.

This complicated definition shall be analyzed by two examples. The first deals with the molecule trans-dichloro ethylene. By considering the molecular geometry one can identify the different symmetry elements that form the point group $C_{2h}$. The corresponding character table is illustrated in Table 3.3 that contains two additional columns for our purpose of calculating the dimension as given above.

To start with, one can first calculate the trace for a given symmetry element. This simplifies the calculation since one only needs to consider the characters for the E and $\sigma_h$ symmetry elements. For the calculation of the dimension than one has $h_i \equiv 1$ since there are only A and B terms present. For $h_k \equiv 1$ and $h \equiv 4$. From this, the corresponding dimensions are calculated. As a check, the sum of all dimensions has to equal 3N for N the number of atoms. The last column, the proper vibrations are then calculated by subtracting the rotations and vibrations for a given symmetry type. The last step then involves the assignment of the $A_g$ and $B_g$ types to Raman-active, and the $A_u$ and $B_u$ types to IR-active vibrations according to the occurrence of the corresponding elements in the sixth and seventh column.
Table 3.4: The character table for the group $D_{3d}$.

<table>
<thead>
<tr>
<th>$D_{3d}$</th>
<th>3m</th>
<th>E</th>
<th>2C3</th>
<th>3C2</th>
<th>i</th>
<th>2S0</th>
<th>3σ_d</th>
<th>proper vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>1</td>
<td>1</td>
<td>-3</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>$E_g$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>(X, Y)</td>
<td>8</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>$E_u$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
<td>(X, Y)</td>
<td>8</td>
</tr>
</tbody>
</table>
| trace    | 24 | 0  | 0   | 0   | 0 | 4   |       | 24
|          |    |    |     |     |   |     |       | 18               |

The second example deals with a higher symmetric molecule, ethane. All symmetry elements are combined in the character table for group $D_{3d}$. Here we encounter both two-fold degenerate symmetry types (E) as well as numbers in front of the symmetry elements for the presence of multiple $C_2$ groups for example.

For the calculation of the dimension, we first calculate the trace so that we only need to consider the characters of E and $\sigma_d$. For the dimension, $h \equiv 12$ and for $h_i$ and $h_k$ the values are not uniformly 1. For the E terms $h_i = 2$ and, e. g., $h_k = 3$ for $\sigma_d$. The sum of all dimensions has to equal 24. After subtracting the contributions from rotation and translation we obtain the proper vibrations. It should be emphasized here, that for the symmetry type $A_{1u}$ we have one proper vibration which, however, cannot be detected by either IR- or Raman-spectroscopy. For point groups containing the inversion element, it can be stated that vibrations are either IR- or Raman-active (together with possible non-active vibrations). For other point groups without inversion this doesn’t have to be the case.

With these calculations we have shown that one can directly assign vibrations to IR- or Raman-active modes without the need of calculating the transition dipole moment.

3.5 Questions for Recapitulation

1. Verify the calculation of the $2p_x$ and $2p_y$ wave function according to

$$\psi_{2p_x} = \frac{1}{\sqrt{2}} (-\psi_{2p,1} + \psi_{2p,-1})$$  \hspace{1cm} (3.62)

$$\psi_{2p_y} = \frac{i}{\sqrt{2}} (\psi_{2p,1} + \psi_{2p,-1})$$  \hspace{1cm} (3.63)

2. Calculate the term symbol for sulfur, iron, and uranium in the ground state!
3. Calculate the IR- and Raman-active vibrations for the water molecule (point group $C_2v$).

3.6 References

general:
Chapter 4

Nuclear Magnetic Resonance
(NMR)

4.1  Introduction

1896 Pieter Zemmann observed the splitting of optical lines in the presence of a magnetic field. Therefore, all splitting due to a magnetic field are referred to as the 'Zeeman effect'. In the megahertz and gigahertz range of the electromagnetic spectrum, these are related to energy splittings of nuclear spins or electron spins. The latter, discovered 1944 by Jevgeni Konstantinovich Savoiski is called electron paramagnetic resonance (EPR) or electron spin resonance (ESR), that will be the subject in the next chapter. 1945 the groups of Edward Mills Purcell in Boston and of Felix Bloch at Stanford did the first successful experiments on nuclear magnetic resonance (NMR).

Nuclear magnetic resonance discussed here has to be differentiated from nuclear resonance discussed in chapter 9. Nuclear resonance deals with transitions between nuclear ground and excited states at very high frequencies of $\gamma$-rays and is experimentally dealt with in Mößbauer spectroscopy.

4.2  Basics of NMR

In NMR, the subject of interest is the nuclear spin and transitions between nuclear spin states. The spin quantum number $I$ is related to the spin angular momentum
CHAPTER 4. NUCLEAR MAGNETIC RESONANCE (NMR)

by

\[ |\vec{L}| = \hbar \sqrt{I(I+1)} \]  \hspace{1cm} (4.1)

With the external magnetic field by definition oriented in the z-direction quantization along this axis exists.

\[ L_z = I_z \hbar \equiv m \hbar \]  \hspace{1cm} (4.2)

with \( m \) being the magnetic quantum number which can take \( 2I + 1 \) values.

\[ m = -I, -I + 1, \ldots, I - 1, I \]  \hspace{1cm} (4.3)

The derivation of the spin quantum numbers for all isotopes is exactly only possible with the help of nuclear physics. Nevertheless, three simple classifications are useful:

• \( I \) is half-integer for odd mass numbers

• \( I \) is a whole number for even mass and odd proton numbers

• \( I \) is zero if both mass and proton numbers are even

From this, the properties of some common isotopes can be obtained. For instance, \(^{12}\text{C}, ^{16}\text{O} \) or \(^{28}\text{Si}\) have \( I = 0 \) and cannot be detected with NMR. More common nuclei are \(^1\text{H} \) (\( I = \frac{1}{2} \)), \(^{13}\text{C} \) (\( I = \frac{1}{2} \), natural abundance 1.1%), \(^{14}\text{N} \) (\( I = 1 \), \(^{27}\text{Al} \) (\( I = \frac{5}{2} \) or \(^{31}\text{P} \) (\( I = \frac{1}{2} \)). For reasons that will become clear later, systems with spin \( I = \frac{1}{2} \) can be treated simpler, since only two energy levels are involved and no quadrupolar coupling is present.

In analogy to the classical description, a nucleus with spin creates a circular current which produces a magnetic moment \( \vec{\mu} \). This will create a torque in the presence of an external magnetic field

\[ \vec{T} = \vec{\mu} \times \vec{B} \]  \hspace{1cm} (4.4)

with the energy being defined as

\[ E = -\vec{\mu} \cdot \vec{B} \]  \hspace{1cm} (4.5)
4.2. BASICS OF NMR

The gyromagnetic (better: magnetogyric) ratio $\gamma$ is a specific constant for each isotope and is related to the magnetic moment via

$$\vec{\mu} = \gamma \vec{L}$$ \hfill (4.6)

with the z-component then being

$$\mu_z = \gamma L_z = \gamma I_z \hbar = \gamma m \hbar$$ \hfill (4.7)

From this, the resulting energy (the energy difference to the case of absent magnetic field) is obtained

$$E_m = -\mu_z B_0 = -\gamma m \hbar B_0$$ \hfill (4.8)

The magnetic field is generally defined as $\vec{B} = (0, 0, B_0)$. In the case $I = \frac{1}{2}$ we have to two values $m = \pm \frac{1}{2}$ and the energy difference is

$$\Delta E_{-\frac{1}{2}, \frac{1}{2}} = \gamma \hbar B_0 = \hbar \omega_L$$ \hfill (4.9)

This is illustrated in Figure 4.1.

![Energy diagram for a spin-$\frac{1}{2}$ system.](image)

Figure 4.1: Energy diagram for a spin-$\frac{1}{2}$ system.

$\omega_L = \gamma B_0$ is the Larmor-frequency that is the central equation of NMR. It states that for every isotope we have a characteristic NMR frequency which makes NMR
an element-selective detection technique. Additionally, the frequency is proportional
to the external magnetic field. Typical field strengths range from 2.4 to 24 T which
yield, e. g., for $^1H$ frequencies between 100 and 1000 MHz.

While $I_z$ is quantized, $I_x$ and $I_y$ are not. Therefore, all nuclear spins are arranged
oriented on a cone either in the direction of the magnetic field are opposing it
(orientation of $m = \pm \frac{1}{2}$ depending on the sign of $\gamma$) precessing around it. For many
considerations it is advantageous to consider and calculate the sum of all nuclear
spins, the macroscopic magnetization $M_0$. This can be calculated via

$$M_0 = N\gamma \hbar \int_{m=-I}^{m=+I} \frac{m e^{\gamma m B_0/(kT)}}{e^{\gamma m B_0/(kT)}} = \frac{N\gamma^2 \hbar^2 I(I + 1)}{3kT} B_0 \quad (4.10)$$

In the derivation the following sums are taken into account: $\sum 1 = 2I + 1$, $\sum m = 0$,
$\sum m^2 = \frac{I(I+1)(2I+1)}{3}$.

With $M_0 = \chi_0 H_0 = \frac{\omega_0 B_0}{\mu_0}$ (see chapter 2.1) this is directly related to the Curie
law $\chi = \frac{C}{T}$.

Spontaneous transitions can be neglected due to the low frequencies and prob-
babilities for absorption and induced emission are equal. Absorption or emissions
occurs if the two occupation numbers are different. To get an estimate of the sensi-
tivity of an NMR experiment, consider the Boltzmann distribution

$$\frac{N_{\frac{1}{2}}}{N_{-\frac{1}{2}}} = e^{\frac{\hbar \gamma B_0}{kT}} = e^{\frac{\hbar \omega_L}{kT}} \quad (4.11)$$

If the take for example $\omega_L = 2\pi 500MHz$ and $T = 300K$, we obtain for $\frac{\hbar \omega_L}{kT} \approx 8 \cdot 10^{-5}$. Therefore the exponential function can be expanded to the linear term
(Taylor expansion, chapter 10.1) and we obtain for the difference in populations

$$\frac{N_{\frac{1}{2}} - N_{-\frac{1}{2}}}{N_{-\frac{1}{2}}} = \frac{n}{N_{-\frac{1}{2}}} \approx \frac{\hbar \omega_L}{kT} = 8 \cdot 10^{-5} \quad (4.12)$$

with $n$ being the difference in occupation numbers. As this is a fairly small number,
NMR is practically a very insensitive measurement. Saturation can easily be reached
by the application of a continuous rf-field of the corresponding frequency. $n$ can
be increased (apart from larger sample amounts) by lowering the temperature or
increasing the magnetic field.
4.3 Experimental Setup

Though the setup of NMR spectrometers can vary, in general the following components as given in Fig. 4.2 are generally present.

![Diagram of NMR spectrometer components](image)

Figure 4.2: General components of an NMR spectrometer.

The critical point is the separation of pathways for the radio frequency going to the NMR coil and the resulting induced voltage coming from the sample to be collected. Since the ingoing power can be 6-8 orders of magnitude larger, an efficient separation is necessary. Due to the low voltage as the response from the sample (on the order of micro- to nanovolts), the signal is usually amplified before going to the computer for analysis.

To differentiate are cw (continuous wave) and pulse spectrometers. In cw spectrometers the frequency (or magnetic field) are varied continuously. As this is time-consuming, almost all spectrometers today are pulse spectrometers where a short radio frequency (rf) pulse excites the whole spectrum at a time and then the induced voltage is collected as a function of time, called free induction decay (FID). The flip angle of a given pulse is defined as \( \theta = t_p \omega_1 = t_p \gamma B_1 \) with \( \omega_1 \) being the radio frequency and \( B_1 \) the radio frequency field. The corresponding pulses are then named \( \pi/2 \) or \( \pi \)-pulses.

4.4 Relaxation

Though not classically a spectroscopy, relaxation plays an important role in NMR. Because of the Fourier pair time and frequency, a given relaxation time always refers
to a frequency that can be correlated with the properties of matter. Therefore, we will discuss the different relaxation times in NMR and how they are determined.

4.4.1 Spin-Lattice Relaxation

The spin-lattice relaxation $T_1$, also longitudinal relaxation time, is the one related to the lifetime of the excited state. The term longitudinal refers to orientation of the macroscopic magnetization along the $z$-axis. If one considers disturbance of the equilibrium magnetization, the regeneration of equilibrium follows the spin-lattice relaxation. In this process energy has to be given away from the spin-system to the outside (oscillations, rotations, translations, external fields) which is generally called ‘lattice’ (not to be confused with, e.g., the crystal lattice system).

For switching on or off of a magnetic field (rarely done in practice) the following equations hold

\[ n = n_0 \left( 1 - e^{-\frac{t}{T_1}} \right) \]  
\[ n = n_0 e^{-\frac{t}{T_1}} \]

with $n$ denoting the difference in occupation numbers ($n_0$ for equilibrium).

For the experimental determination of $T_1$ we have to know that populations cannot be determined directly with NMR. Observable magnetization is only that which is oriented in the xy-plane so that a voltage can be picked up in the detection coil. For this, mainly two pulse sequences are in use, Inversion Recovery (IR) and Saturation Recovery (SR).

For the first (IR), a $\pi$ pulse is applied to invert magnetization from the $z$ to the -$z$ axis. After this, the system wants to regain equilibrium magnetization. In separate experiments with variable delay after the $\pi$ pulse, the magnetization is converted to the xy-plane via a $\frac{\pi}{2}$ pulse. Plotting the signal intensity (FID or spectrum) as a function of this variable delay then yields the following curve (Fig. 4.3) that can be fit using the equation

\[ M(t) = M_0 \left( 1 - 2e^{-\frac{t}{T_1}} \right) \]

A characteristic point is where the magnetization is zero, which directly yields $	au = T_1 \ln 2$. 

4.4. RELAXATION

Figure 4.3: Signal intensity as a function of delay in the inversion recovery experiment. The line is the fit using equation 4.16.

The saturation recovery sequence works in a similar way, but instead of the π pulse it uses a set of $\frac{\pi}{2}$ pulses with intermittent delays to effectively destroy z-magnetization. The rest of the sequence is identical and the curves follows that of the inversion recovery experiment from the point $M(t) = 0$. The fitting function therefore is

$$M(t) = M_0 \left(1 - e^{-t/T_1}\right)$$

(4.17)

The choice of sequence is in principal arbitrary. Nevertheless, the saturation recovery sequence is faster since one does not need to wait between consecutive experiments (delay times) for the system to regain equilibrium which in principle requires rough knowledge of the $T_1$. On the other hand the inversion recovery is more accurate since it spans a larger time scale.

4.4.2 Spin-Spin Relaxation

The induced signal or voltage in the detection coil decays with another relaxation time constant, $T_2$, the spin-spin relaxation or transverse relaxation time. Practically, there is also a contribution from external magnetic field inhomogeneities that leads to a faster decay. For this, the actual decay is often named $T_2^*$ with the 'real' $T_2$ being due to the sample with $T_2^* < T_2$.

Signal decay is a consequence of the loss of 'coherence'. This term documents that after an initial $\pi/2$ pulses the phases of all nuclei are identical to the phase of the
radio frequency pulse. After the pulse, interactions between the nuclei (see below) leads to slightly different magnetic fields for the different nuclei and consequently the phase relation is lost, called ‘dephasing’.

To measure the spin-spin relaxation time, we usually can’t use the exponential decay of the FID since it decays with $T_2^*$. Two other possibilities can be used instead (keeping in mind that for both experimental uncertainties still can lead to smaller observed values). The first, is called ‘Hahn-echo’, named after Erwin Hahn developed in 1950 [1].

In the Hahn-echo after a $\frac{\pi}{2}$-pulse to transfer magnetization into the xy-plane dephasing occurs during a period $\tau$. This means that some spins precess at a higher or lower frequency than the resonance frequency. Afterwards, a $\pi$-pulse inverts the spins in the xy-plane. After another time $\tau$ all spins converge together at the same point and form an ‘echo’. An illustration is given by the 'Rennbahn-echo' (Fig. 4.4).

![Figure 4.4: Illustration of the Hahn-echo.](image)

To determine the spin-lattice relaxation time, multiple experiments with different echo times $2\tau$ have to be run and the resulting curve fitted to a decreasing exponential. A faster method is the CPMG-sequence (named after Carr-Purcell-Meiboom-Gill) which produces repeat echoes by multiple $\pi$-pulses as illustrated in Fig. 4.5. With this, the full curve can be observed within one experiment, though spectroscopic resolution is lost.
4.4. RELAXATION

4.4.3 Bloch Equations

Felix Bloch set up phenomenologically the effects of relaxation times $T_1$ and $T_2$ on the magnetization. For this, he defined an effective magnetic field

$$B_{\text{eff}} = (B_{rf}, 0, B_0 - \frac{\omega}{\gamma})$$  \hspace{1cm} (4.18)

Additionally, to the external static magnetic and radiofrequency field he added the resonance offset $\omega_L - \omega$ to include the effect when the radiofrequency deviates slightly from the Larmor frequency. For the time dependence of the magnetization we can write

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}_{\text{eff}} - \frac{M_x \vec{e}_x + M_y \vec{e}_y}{T_2} - \frac{(M_z - M_0) \vec{e}_z}{T_1}$$ \hspace{1cm} (4.19)

with $T_1$ being effective on the z-component and $T_2$ on the x- and y-component of the magnetization.

In the stationary case ($d\vec{M}/dt = 0$) we get the solution

$$M_x = \frac{(\omega - \omega_L)T_2^2}{1 + (\omega - \omega_L)^2T_2^2 + \gamma^2 B_{rf}^2T_1T_2} \gamma B_{rf} M_0$$ \hspace{1cm} (4.20)

$$M_y = \frac{1}{1 + (\omega - \omega_L)^2T_2^2 + \gamma^2 B_{rf}^2T_1T_2} \gamma B_{rf} M_0$$ \hspace{1cm} (4.21)

$$M_z = \frac{1}{1 + (\omega - \omega_L)^2T_2^2 + \gamma^2 B_{rf}^2T_1T_2} M_0$$ \hspace{1cm} (4.22)

These equations simplify if one uses weak rf-fields to prevent saturation. For this case $\gamma^2 B_{rf}^2 T_1T_2 \ll 1$ and one obtains:

$$M_x = \frac{(\omega - \omega_L)T_2^2}{1 + (\omega - \omega_L)^2T_2^2} \gamma B_{rf} M_0$$ \hspace{1cm} (4.23)
CHAPTER 4. NUCLEAR MAGNETIC RESONANCE (NMR)

\[ M_y = \frac{T_2}{1 + (\omega - \omega_L)^2 T_2^2} T_1^r B_{rf} M_0 \]   \hspace{1cm} (4.24)
\[ M_z = M_0 \]   \hspace{1cm} (4.25)

4.4.4 Further Relaxation Times

In principle, further relaxation times can be defined. One more frequently used one is called \( T_{1\rho} \) or spin-lattice relaxation in the rotating frame. Here, one measures the signal decay when radiofrequency pulses of different lengths are applied. The magnetization can be ‘spinlocked’ along an axis in the xy-plane and decay is slower than without the pulse. Nevertheless, because of the much higher external magnetic field \( B_0 \) finally the magnetization vector will orient along the z-axis again. Clearly, \( T_{1\rho} \) depends on the applied radiofrequency power and given values are of no information content without this additional value.

In general, the study of relaxation times allows to determine frequencies of motion of the material under study. Due to the direct relation between time and frequency (Fourier pair) relaxation times are a direct measure of frequency. \( T_1, T_{1\rho}, \) and \( T_2 \) can span several orders of magnitude from microseconds to seconds and therefore enable to probe different motions in frequency ranges from Hz to MHz.

The sources of relaxation are due to internal interactions within the material of study which also have effects on the NMR spectrum that will be discussed in the next section.

4.5 Interactions

This sections deals with the characteristic interactions in NMR spectroscopy that are responsible for the resulting spectra. They also provide a mechanism for relaxation, something that won’t be discussed here.

4.5.1 Chemical Shift

As mentioned in the previous chapter, the nucleus is shielded by the surrounding electrons. This shielding is a result of an opposing current generated in the electrons.
Therefore, the nucleus (or nuclear spin) experiences a slightly different magnetic field from the external one.

\[ B_{\text{loc}} = (1 - \sigma)B_0 \] (4.26)

Because of the relation of the shielding to the chemical bonds, this interaction is called chemical shift.

In fact \( \sigma \) is not a scalar constant but a tensor which is immediately apparent from the fact that the orientation of a molecule with respect to the magnetic field will produce anisotropic shielding effects (called chemical shift anisotropy, CSA). For solution NMR, however, the Brownian motion averages all anisotropic effects and an isotropic chemical shift remains. Historically, shielding effects are called diamagnetic (from s-orbitals) and paramagnetic (from p- or other orbitals), though these terms might be confusing since they can both be present in diamagnetic samples.

The absolute shielding values (with respect to the bare nucleus) can be calculated, but experimentally this is hard to perform. Therefore referencing with a known substance is in use which accounts for the small differences due to the local internal fields.

\[ \delta = \sigma_{\text{reference}} - \sigma \] (4.27)

For \(^1\text{H}, ^{13}\text{C}, \) and \(^{29}\text{Si}\) the officially named reference compound is TMS (tetramethylsilane). This also makes shift values given in ppm (parts per million) independent of the magnetic field and allows for tabulation of shifts for numerous compounds in databases. Since the chemical shift is a result from the electronic surrounding of the nuclear spin, it is clear that this is a precise information for the assignment of unknown structures. Typical shift values can directly be related to functional groups. Even calculations predict values remarkably good (at least for solution NMR). Therefore the determination of the chemical shift of a compound is of very high importance.

The electron spin also influences the NMR frequency of a given nucleus. In diamagnetic samples due to pairing of electron spins due to the Pauli principle this effect vanishes. Nevertheless in materials with lone electrons, like metals, superconductors, paramagnetic compounds, huge effects on the chemical shift are observed which are referred to as Knight-shift. Prediction of Knight shifts is more complicated and also shows a strong temperature dependence. Calculation of shifts is also more complicated. Nevertheless, this interaction gives detailed information about
the electronic structure. In solution NMR, sometimes paramagnetic salts are added to detect resonances (spins, atoms) close to these salts as they show a remarkable shift (‘paramagnetic shift reagents’).

4.5.2 Indirect Dipolar Coupling

Next to the chemical shift, this interaction is the most important in solution NMR. Besides the term indirect dipolar coupling also $J$-coupling or spin-spin coupling is used. It derives from the fact that magnetic dipoles (nuclear spins) interact via bonding electrons. Different couplings are illustrated by a symbol

\[ J_{AX} \] (4.28)

Here, $n$ denotes the number of chemical bonds between the coupling partners and $A$ and $X$ denote the involved nuclei, e.g., HH or HC.

This interaction is independent of the external magnetic field, values for the splitting of the lines are usually given in Hertz [Hz]. Differentiation between signals from chemical shift or spin-spin coupling is therefore possible via changing the magnetic field. Equivalent nuclei don’t show a spin-spin coupling. If nuclei are equivalent can be obtained from consideration of the symmetry of the molecule together with taking into account free rotation of organic molecules about single bond (e.g., C-C bond). There is a differentiation between chemical equivalence and magnetic equivalence. The above described case means chemical equivalence. Magnetic equivalence exists if nuclei that have the same chemical shift show only one spin-spin coupling to a neighboring group.

For example, the $^1$Hs in difluoromethane, $\text{CH}_2\text{F}_2$, and those in the methyl group of ethanol are equivalent. This is not the case for the $^1$Hs in 2,2'-difluoroethene, $\text{C}_2\text{H}_2\text{F}_2$, because the distances between the different nuclei are not the same.

To explain the observed splittings due to $J$-coupling we consider a $^1J_{AX}$ system. We denote the $m = +\frac{1}{2}$ state by $\alpha$ and the $m = -\frac{1}{2}$ by $\beta$. Then, the $\alpha\alpha$ state is energetically lowest and $\beta\beta$ highest. The two mixed terms $\alpha\beta$ and $\beta\alpha$ lie between them and are only identical if a homonuclear system is considered. For an uncoupled system, we obtain two lines since only transitions of one spin only can normally be observed with NMR.
4.5. INTERACTIONS

For the illustration of the energy shifts due to $J$-coupling we have to consider the corresponding electron spin involved in the chemical bond, see Fig. 4.6. The general requirement is that the two electron spins - since belonging to the same orbital - have to have opposite spin. A parallel orientation of electron and nuclear spin is energetically preferred. For the $\alpha\alpha$ system an antiparallel orientation leads to an increase of the energy level (the same is true for the $\beta\beta$ system). For the mixed systems, a parallel orientation of electron and nuclear spin can be fulfilled for both nuclei, which leads to a reduction in energy. For the coupled system, this results in an energy diagram shown in Fig. 4.7.

![Figure 4.6: Illustration of $J$-coupling of two nuclei including electron spin orientation.](image)

Together with the given transition energies, we obtain a doublet for each nucleus with a separation of the spin-spin coupling constant $J$ which is identical for the coupled spins and therefore allows for assignments of coupled functional groups in the NMR spectrum.

For a given number of equivalent coupled spins we then obtain doublets, triplets, quartets, ... with the intensities according to Pascal’s triangle, shown in Fig. 4.8.

Clearly, if there are many different $J$ couplings (even if they are only different by 0.1 Hz), the coupling schemes can become very complicated. For quadrupolar nuclei, Pascal’s triangle is not valid. For example, $J$-coupling to a $^2\text{H}$ (I=1) yields for one coupled $^2\text{H}$ to a triplet with intensities 1:1:1 due to the three magnetic states $m=1$, $m=0$, and $m=-1$.

So the combination of chemical shifts for identification of functional groups, the indirect dipolar coupling identifies which functional groups are coupled to each other and allow assignment of the arrangement of functional groups in the molecule.
Figure 4.7: Energy levels and resulting NMR spectrum for uncoupled and coupled system.

\[ \omega = \gamma (B_0 + B_{z\text{local}}) \]  

(4.29)

4.5.3 Direct Dipolar Coupling

Next to the indirect dipolar coupling there is also a direct dipolar coupling which involves to coupled dipoles that interact through space and no chemical bond is required. One can easily understand that a magnetic dipole (a nucleus with magnetic moment) creates a small extra local magnetic field at a neighboring nucleus. Therefore we obtain a slightly different resonance frequency
Mathematically, this frequency shift can be calculated as

$$\Delta \omega \propto \pm \frac{\gamma_1 \gamma_2 \hbar}{r_{12}^3} (3 \cos^2 \theta - 1) \quad (4.30)$$

There are different prefactors for differentiating homonuclear ($\gamma_1 = \gamma_2$) and heteronuclear couplings ($\gamma_1 \neq \gamma_2$). Important here is the inverse cube dependence of the distance $r$ between the spins which indicates that the size of the dipolar couplings reduces rapidly with increasing distance and the angle $\theta$ which indicates the angle between the external magnetic field and the internuclear vector.

The latter has many consequences: for a liquid sample with Brownian motion, rapid tumbling of the molecules eliminates the direct dipolar coupling that doesn’t show up the NMR spectrum. Mathematically, the dipolar coupling (as also the chemical shift and principally the $J$-coupling) are tensorial interactions with the dipolar coupling being a traceless tensor in opposition to the other two interactions). In single-crystals, the splitting of the resonance line strongly depends on the angle $\theta$. By varying the orientation of the crystal with respect to the magnetic field this interaction can be quantified and the distance between spins be determined very exactly. In many solid samples, however, there is polycrystalline or even amorphous material present with all different orientations $\theta$. This leads to a characteristic broadening of the line which can be calculated (‘powder pattern’ or ‘powder average’) and the distance determined. Most prominent problem is the fact that all nuclei are coupled with each other which soon complicates a spectrum beyond a point where analysis is possible.

### 4.5.4 Quadrupolar Coupling

The discussion of quadrupolar coupling is often omitted since it is only present for nuclei with a spin quantum number $I > \frac{1}{2}$ and the fact that serious complications to the NMR spectra are possible. We will therefore only briefly touch this aspect.

Due to a non-spherical charge distribution in the nucleus, for spins with $I > \frac{1}{2}$ a quadrupolar moment results. This interacts with an electric field gradient that is generated by the surrounding nuclei and electrons of neighboring atoms. An electric field gradient (EFG) results if the symmetry around the spin of interest is non-spherical, i.e., for exact octahedral or tetrahedral symmetry, no EFG is present.
The electric field gradient can be obtained from the second derivative of the electric potential

\[ q_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j} \]  

(4.31)

The quadrupolar interaction is also a traceless tensor so its effects don’t show up in solution NMR. Characteristic value is the quadrupolar coupling constant

\[ \nu_Q = \frac{3e^2 Qq_{zz}}{2I(2I - 1)\hbar} \]  

(4.32)

which leads to a frequency splitting of

\[ \Delta \nu_Q = \frac{1}{2} \nu_Q \left[ 3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\phi \right] \]  

(4.33)

\( \eta \) defines the asymmetry parameter

\[ \eta = \frac{q_{yy} - q_{xx}}{q_{zz}} \]  

(4.34)

and indicates the deviation from axial symmetry of the EFG. \( \theta \) and \( \phi \) are defined in a similar way as the spherical coordinates 10.4.

In a similar way to the dipole coupling, energy level shifts are obtained, see Fig. 4.9.

In the spin-\( \frac{3}{2} \) system it can be seen that the central transition \( \frac{1}{2} \leftrightarrow -\frac{1}{2} \) is not affected by quadrupolar coupling. This is only true as long as the quadrupolar interaction is small with respect to the external magnetic field. This however, is not always the case, coupling constants exceeding 20 MHz are known that also lead to a shift of the frequency for the central transition. Mathematically this means that the interaction cannot be treated as a small perturbation to the Zeeman interaction (1st order perturbation theory), but as a larger one which requires 2nd order perturbation theory. The details, however, are beyond the scope of this course.

### 4.6 Experimental Flexibility

Due the different interactions NMR spectra can become quite complicated and hard to analyze. Nevertheless, the strength of the NMR technique is that due to variation of the measurements certain interactions can be eliminated and therefore the analysis...
simplified. Some examples will be discussed in this section. There are two principal ideas, one is to do mechanical modifications and the other one is the use of a suitable combination of pulses and delays (multipulse approach).

4.6.1 MAS

As was described for dipolar and quadrupolar coupling, there is an angular dependence of the splitting. A similar effect is also existing for the chemical shift anisotropy. All these interactions contain the angular term $3\cos^2\theta - 1$. By aligning
CHAPTER 4. NUCLEAR MAGNETIC RESONANCE (NMR)

a sample along an angle

\[ \arccos \frac{1}{\sqrt{3}} \approx 54.74^\circ \] 

(4.35)

this interaction should vanish. There is an additional requirement for sample rotation (nowadays up to 70 kHz, driven by air flows) in order to align - in time average - e. g. the internuclear vector along this so-called 'magic angle'.

If the spinning speed is high enough, chemical shift anisotropy (CSA), dipolar coupling and 1st order quadrupole coupling can be eliminated. If the spinning speed is not high enough, resolution improvement are still possible, just a number of rotational (spinning) sidebands appear at multiple of the rotation frequency in the spectrum, see example in Fig. 4.10. The envelope of the spinning sidebands contains information about the corresponding interaction.

![Figure 4.10: $^{13}$C static and MAS spectra of the carboxylic carbon of glycine.](image)

4.6.2 Decoupling

A frequently used technique in NMR is spin decoupling. In a crowded J-coupled spectrum the isotropic peaks cannot simply be assigned. By continuous irradiation
of a neighboring nucleus at its resonance frequency during detection removes the coupling due to a permanent level transitions. This is often done for $^{13}$C detection with $^1$H decoupling, but in principal can also be done between $^1$Hs of different frequency though one has to be careful with the excitation bandwidth of the continuous pulse. Both direct and indirect dipolar coupling are affected by decoupling.

4.6.3 Double Resonance

Double resonance in principle means the irradiation of two frequencies at the same time. In a more strict sense, irradiation of two Larmor frequencies for two different types of nuclei, e. g. $^1$H-$^{13}$C, is meant. With this technique magnetization [coherence] transfer between the two spin systems is possible that can lead to signal enhancement but can also be used to identify signals deriving from nuclei in close proximity.

4.6.4 2D NMR

In general multidimensional NMR is a useful tool to separate NMR interactions (e. g., $J$-couplings and isotropic chemical shifts) or to deduce connectivities between signals that help in assignment of unknown structures.

Almost every 2D NMR pulse sequence can be separated into four phases:
- preparation - evolution - mixing - detection

Evolution and detection are mainly time delays that are given the time variables $t_1$ and $t_2$, respectively. These two time domains are later Fourier transformed in the frequency axes $F_1$ and $F_2$, respectively. The detection is named the direct dimension since in general an FID is recorded. For the indirect dimension ($t_1$), a stepwise increment is done between successive FIDs to simulate a time dimension with a dwell time. In practice this leads to a modulation of the directly detected FID. For preparation and mixing in the simplest case two $\frac{\pi}{2}$ pulses are sufficient as in the COSY (correlation spectroscopy) experiment.

The resulting 2D spectrum, shown in Fig. 4.11, contains diagonal elements for magnetization that during $t_1$ and $t_2$ didn’t change its frequency and off-diagonal elements indicating correlations since the frequency during $t_1$ is different from that during $t_2$ because of a $J$-coupling interaction between the two coupled spins.
CHAPTER 4. NUCLEAR MAGNETIC RESONANCE (NMR)

Figure 4.11: Principal look of a H-H COSY experiment.

Many more combinations of pulses are possible, specifically designed for the question of interest. In the same way as going from a 1D to a 2D experiment, further dimensions can be created, though the time necessary for the measurement increases significantly with every dimension.

4.6.5 Magnetic Resonance Imaging

Though practically not a spectroscopy, we nevertheless want to briefly introduce the principles of magnetic resonance imaging which has a very high impact in medicine.

2D and 3D images of (parts of) the human body mainly reflect the density of water in certain areas. Therefore, bones are represented as black elements. The main idea of imaging is to have spatial resolution, i.e., a recorded frequency is directly related to the position. For this, one has to create a well-defined inhomogenous
magnetic field. This is done by external magnetic field gradients which is done by gradient coils. If, for example, a gradient is given in x-direction, then the magnetic field is given as

\[ B(x) = B_0 + x \cdot G \]  

(4.36)

with G being the gradient strength. Because of \( \omega = \gamma B \) a given x-coordinate will have a different frequency. This can in principal be done for all three dimensions but practically there are also different gradients (phase gradients) used where the phase of the signal indicates position for another direction. Then there are different techniques existing to scan the 3D space more efficiently and faster which is more a mathematical question of optimization.

The spin density image can be further modified by using contrasts like differences in \( T_1 \) and \( T_2 \) relaxation times. Even the correlation between certain movements or actions with activity in certain areas of the brain is possible (known as fMRI or functional MRI). Here one uses the fact that hemoglobine present in the blood to transport oxygen contains paramagnetic iron that influences strongly the relaxation time. A high blood flow is then indicated by a strong decrease in relaxation time, known as BOLD effect (blood oxygen level dependent). Many other useful applications of MRI such as quantifying blood flow in arteries show the importance of this technique in modern medicine.

4.7 References

general:
Chapter 5

Electron Spin Resonance (ESR)

5.1 Introduction

Similar to NMR, electron spin resonance (ESR) - sometimes also named electron paramagnetic resonance (EPR) - deals with the splitting of the electron spin states in an external magnetic field. The first experiment was done 1944 by Jewgeni Sawoiski at a magnetic field of 4.76 mT at a frequency of 133 MHz on a sample of copper(II) chloride dihydrate. The existence of the electron spin was already demonstrated before by the magnificent experiment by Stern and Gerlach (cf. chapter 3.3).

For ESR experiments to be possible, the existence of an atomic or molecular magnetic moment is necessary. This requires the existence of unpaired electrons or non-filled electron shells. For paired electrons due to the Pauli principle the two electrons in an orbital have to have opposite spin and the moment is zero. This limits the number of molecules and materials that can be investigated. These can be categorized into

- free radicals, such as ·CH₃
- transition metal ions with non-filled d or f orbitals
- defects in solids. Crystal imperfections might leave a point which contains just an electron or other ways with a partially filled electron orbital
- ions with a non-bonding s-electron, such as Ga²⁺
systems with more than one unpaired electron, such as triplet states (e.g. $O_2$). These states can in principal also be generated via photoirradiation.

- atoms with non-filled electron shells, such as atomic hydrogen or NO

- metals and semiconductors, which have unpaired electrons in the conduction band

The major difference between NMR and ESR is the fact that the electron has both spin and orbit and their interaction has to be taken into account. Therefore, in opposition to NMR - there is no direct relation between spin and resonance frequency.

5.2 Experimental Setup

EPR spectrometers are mainly continuous-wave (cw) spectrometers. They work at fixed frequencies that are named by characters and the magnetic field is varied. Typical frequencies are the X-band at 9.5 GHz and a magnetic field of 0.3 T, the Q-band at 36 GHz and a magnetic field of 1.2 T, or the W-band at 95 GHz and a magnetic field of 3.5 T. These magnetic fields are still quite low so that electromagnets can be used. The frequencies are in the microwave range with wavelength on the order of a few millimeter.

The typical setup of an ESR spectrometer is shown in Fig. 5.1.

The clystron is a frequency and power stabilized frequency synthesizer. Important in the setup is the circulator which sends the power to the sample and the reflected power from the sample to the detector. Transmittance of the microwave frequency is done by waveguides that are rectangular tubes with the diameter equal to the wavelength of the microwave. The other equipment is similar to the NMR setup.

The magnetic field is swept linearly according to the formula

$$B_0 = B_{\text{initial}} + \text{const} \times t \quad (5.1)$$

Additionally, the magnetic field is modulated by a frequency of typically 100 kHz that is generated by additional coils around the resonator. With that the magnetic
5.2. EXPERIMENTAL SETUP

Figure 5.1: Schematic setup of an ESR spectrometer.

The field can be described as

\[ B_0 = B_{\text{initial}} + \text{const} \cdot t + B_{\text{modulation}} \cdot \sin(2\pi \nu_{\text{modulation}} \cdot t) \]  \hspace{1cm} (5.2)

The modulation frequency should be smaller than the EPR linewidth to prevent falsification but also as large as possible to improve the signal-to-noise ratio. Due to the limited bandwidth of the modulation a signal-to-noise gain is obtained compared to the unmodulated signal. The modulated signal is afterwards demodulated before computer display.

In opposition to NMR, ESR spectra are usually shown in dispersion mode (first derivative of the absorption). By this, structures are easier to recognize as demonstrated in figure 5.2 on the cost of quantitativeness. For the fact that absorption spectra are more common to us, we will only display absorption spectra below.

For pulsed EPR, similar requirements exist as for pulsed NMR. Complications are the broad spectra which complicate full excitation of the spectrum. That means for a 100 MHz linewidth one needs pulses on the order of 10 ns. Additionally, since spin-spin relaxation times are faster than in NMR, resonators with short dead times are needed to record FIDs and echo times for spin echo measurements have to be short. For these reasons, pulse sequences from NMR have to be adapted to ESR and
cannot be directly used. For relaxation time measurements, clearly, pulsed EPR is needed.

5.3 \textbf{g-Factor}

To describe the for ESR very important g-factor, we have to consider both spin and orbit of the electron. An orbiting electron at radius \( r \) with an angular frequency \( \omega \) creates a current \( I = -e\omega/(2\pi) \). The magnetic moment is then \( \vec{\mu} = I\vec{A} \) with \( \vec{A} \) being the enclosed surface being \( A = \pi r^2 \). Then we obtain

\[
\vec{\mu}_L = -\frac{e}{2m_e} L
\]

with \( L = m_e r^2 \omega \) being the angular momentum.

In a similar way we can define the spin magnetic moment for a rotating sphere of mass \( m_e \) and charge \(-e\).

\[
\vec{\mu}_S = -\frac{e}{2m_e} \vec{S}
\]

where \( \vec{S} \) is the electron spin.
5.3. G-FACTOR

$L$ and $S$ are both quantized

$$|\vec{L}| = \hbar \sqrt{l(l+1)} \quad (5.5)$$

$$|\vec{S}| = \hbar \sqrt{s(s+1)} \quad (5.6)$$

The components along the external magnetic field (by definition along the z-axis) are then

$$L_z = l_z \hbar \equiv m_l \hbar \equiv m \hbar \quad (5.7)$$

$$S_z = m_s \hbar \equiv s \hbar \quad (5.9)$$

The Bohr magneton is defined as a combination of different constants that come across the previous definitions

$$\mu_B = -\frac{e}{2m_e} \hbar = 9.274 \cdot 10^{-24} \text{Jm}^2\text{V}^{-1}\text{s}^{-1} \quad (5.11)$$

With that, the magnetic moment can be expressed as

$$|\vec{\mu}| = g \mu_B \sqrt{m(m+1)} \quad (5.12)$$

For orbital magnetism we obtain $g_L = 1$. For the electron spin this is not as simple and requires a relativistic quantum mechanical description. With that one obtains that for the free electron $g = 2.002319304386$.

The total magnetic moment can be obtained from the consideration of Russel Saunders coupling $\vec{J} = \vec{L} + \vec{S}$. Though $\mu_L$ and $\mu_S$ are parallel to their angular momenta, this does not need to be the case for $\vec{M}_J$ and $\vec{J}$, as can be seen in Figure 5.3.

The resulting magnetic moments can then be expressed as

$$|\vec{\mu}_L| = g_L \mu_B \sqrt{L(L+1)} \quad (5.13)$$

$$|\vec{\mu}_S| = g_s \mu_B \sqrt{S(S+1)} \quad (5.14)$$

$$|\vec{\mu}_J| = g_J \mu_B \sqrt{J(J+1)} \quad (5.15)$$

In opposition to NMR, where the chemical shift is only a small change to the resonance frequency (values given in ppm), the ESR analogue, the g-factor, results in huge differences to the resonance frequency. General sizes of ESR interactions will be given in chapter 5.6.
5.4 Zero Field Splitting

An interaction similar to the quadrupolar interaction in NMR exists also in ESR. Since it is also present without magnetic field, it’s called zero field splitting (ZFS). [Quadrupolar interaction known from NMR is also present without magnetic field and can be studied by NQR - nuclear quadrupole resonance]

Consider a Cr$^{3+}$ ion which has three electrons in the 3d shell which are located in three different orbitals. The term symbol therefore is $^4F_{\frac{3}{2}}$, so there is a 7-fold degeneracy of the orbital momentum and 4-fold degeneration of spin. Due to interaction of the d electrons with the electric field of the surrounding ions, for an octahedral ligand field a splitting of the $^4F_{\frac{3}{2}}$ ground state into the point groups $^4A_{2g}$, $^4T_{2g}$, and $^4T_{1g}$, see Fig. 5.4.

In the case of lower symmetry, e. g., axial symmetry (tetragonal), the 4-fold spin degenerated $^4A_{2g}$ state splits up into two states with $M_S = \pm \frac{1}{2}$ and $M_S = \pm \frac{3}{2}$ with an energy difference $\delta$. The remaining 2-fold degeneracy is lifted by an external magnetic field which results in three lines in the ESR spectrum. Without zero field splitting all energy levels would be equally spaced and only one line would result. The three-line spectrum is also referred to as fine structure therefore the zero-field splitting is sometimes also called fine splitting.

Similar to NMR, the zero-field splitting is also orientation dependent so that in
5.5. **HYPERFINE SPLITTING**

solids like single-crystals, the anisotropic nature of the interaction becomes apparent and can be analyzed by recording spectra at different orientations of a single-crystal with respect to the external magnetic field.

### 5.5 Hyperfine splitting

The hyperfine splitting considers the interaction between the electron and a nucleus with spin. Compared to NMR this is similar to a heteronuclear dipolar interaction. It originates from Fermi contact interaction of the s-orbital density (which has a non-zero probability of being at the nucleus) at the nucleus. This interaction has also an anisotropic nature to be identified in solid-state EPR when also p-electrons are involved.

The explanation of hyperfine splitting is that the nuclear spin creates a local
field at the location of the electron.

\[
B_{\text{Local}} = B_0 + a m_I
\]  

(5.16)

with \(a\) being the hyperfine coupling constant. For a nuclear spin \(I = \frac{1}{2}\), the energy scheme in Fig. 5.5 results in an EPR spectrum with two signals split by \(a\).

![EPR Absorption Spectrum](image)

\[\begin{align*}
    m_s = +\frac{1}{2}, m_I = +\frac{1}{2}, & \quad E = +\frac{1}{2} g \mu_B (B_0 + a/2) \\
    m_s = +\frac{1}{2}, m_I = -\frac{1}{2}, & \quad E = +\frac{1}{2} g \mu_B (B_0 - a/2) \\
    m_s = -\frac{1}{2}, m_I = -\frac{1}{2}, & \quad E = -\frac{1}{2} g \mu_B (B_0 - a/2) \\
    m_s = -\frac{1}{2}, m_I = +\frac{1}{2}, & \quad E = -\frac{1}{2} g \mu_B (B_0 + a/2)
\end{align*}\]

Figure 5.5: Energy diagram for hyperfine splitting of an electron with a nuclear spin \(I = \frac{1}{2}\).

Similar to NMR, multiple coupling schemes result for several nuclei and also for nuclear spins with \(I > \frac{1}{2}\).

The hyperfine splitting represents an important interaction in EPR since it allows for the localization of the electron. The term super hyperfine splitting exists for electrons interacting with the nuclear spin of a neighboring atom.

Clearly, there is also electron-electron dipolar interaction. For these, however, we would require two lone electrons that interact without recombination. In an organic molecule with radical at the two ends of the molecule, one could however determine the distance of the electrons and with that for example the size of the molecule.
5.6 Hamilton operators

In this section we briefly describe the principle Hamilton operators of the different interactions in EPR that should only represent in general what the quantum mechanical description looks like. The focus is on the sizes of these interactions given at the end.

- **Zeeman interaction**
  \[
  H_{EZ} = \frac{\mu_B}{\hbar} \vec{B}_0 \cdot g \cdot \vec{S} \tag{5.17}
  \]

- **Zero field splitting**
  \[
  H_{ZFS} = \vec{S} \cdot \vec{D} \cdot \vec{S} = D[S^2_Z - \frac{1}{3}S(S + 1)] + \frac{1}{2}E(S^2_+ + S^2_-) \tag{5.18}
  \]
  The E term hasn’t been explained but stands for the anisotropy of the interaction. \(S_+\) and \(S_-\) are called raising and lowering operators and are defined as \(S_\pm = S_x \pm iS_y\).

- **Dipole-dipole interaction**
  \[
  H_{DD} = \vec{S}_1 \cdot \vec{D} \cdot \vec{S}_2 = \frac{1}{r^3} \frac{\mu_0}{4\pi \hbar} g_1 g_2 \mu_B^2 [\vec{S}_1 \cdot \vec{S}_2 - \frac{3}{r^2} (\vec{S}_1 \cdot \vec{r})(\vec{S}_2 \cdot \vec{r})] \tag{5.19}
  \]
  Compared to the zero field splitting, here the spin operator of two different electrons are considered.

- **Hyperfine coupling**
  \[
  H_{HFI, aniso} = \vec{S} \cdot \vec{T} \cdot \vec{S} \tag{5.20}
  \]

It can be seen that the interactions all have a similar form and all contain tensors in the description identifying the interaction as anisotropic. For solution EPR, some significant simplifications exist similar to NMR.

In opposition to NMR, the sizes of these interactions are strongly different. Whereas in NMR, the Zeeman interaction is by far the largest, in EPR the orbital energy and the splitting in the ligand field exceeds the others. This can be seen in table 5.1.
Table 5.1: Sizes of EPR interactions.

<table>
<thead>
<tr>
<th>interaction</th>
<th>order of magnitude $[cm^{-1}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>orbital energy</td>
<td>$&gt; 10^4$</td>
</tr>
<tr>
<td>energy splitting in ligand fields</td>
<td>$10^2 - 10^4$</td>
</tr>
<tr>
<td>spin-orbit coupling for selected atoms</td>
<td>B: 10, C: 28, F: 271, Cl: 440, Br: 1842</td>
</tr>
<tr>
<td>electron-Zeeman transitions</td>
<td>0.3 (X-band), 1 (Q-band)</td>
</tr>
<tr>
<td>zero field splitting (triplet ground state)</td>
<td>$\approx 1$</td>
</tr>
<tr>
<td>hyperfine interaction</td>
<td>$&lt; 10^{-1}$</td>
</tr>
<tr>
<td>Zeeman transitions of $^1H$ @ 0.7 T</td>
<td>$10^{-3}$</td>
</tr>
</tbody>
</table>

5.7 ENDOR

At the end, we want to discuss one special experiment that involves electron-nuclear interaction and is able to simplify ESR spectra. It is called Electron Nuclear Double Resonance and therefore combines EPR excitation and detection using microwave with nuclear spin irradiation using radio frequencies. It can be understood as detecting NMR transitions via EPR frequencies with the advantage of higher sensitivity compared to NMR but lower than a normal EPR spectrum. Nevertheless, the resolution is higher than in a normal EPR spectrum.

To explain the ENDOR spectrum, consider Fig. 5.6. For EPR the selection rules are $\Delta m_S = \pm 1$ (and $\Delta m_I = 0$). For nuclear spin transitions $\Delta m_I = \pm 1$. For the EPR six lines result all split by the hyperfine interaction constant $a$.

For the ENDOR spectrum, one of the EPR transitions needs to be saturated by a strong microwave field. In Fig. 5.6 this is the transition for $m_I = \frac{1}{2}$. Then a radio frequency sweep on the nuclear side is performed which results in transitions when frequencies $\nu^+$ and $\nu^-$ are reached since the saturation is lifted due to a change of the population of the different states. This difference in occupation numbers produces microwave absorption which is detected and produces only two lines split apart by twice the Larmor frequency. This clearly simplifies the EPR spectrum especially if also other interactions are present at the same time.
5.8 References

general:

Figure 5.6: Energy diagram for the ENDOR experiment for an electron spin interacting with a nuclear spin \( I = \frac{5}{2} \).
Chapter 6

Rotational and vibrational spectroscopy

6.1 Rotational Spectroscopy

Rotational spectroscopy is also called microwave spectroscopy although for small molecules optical methods are also applicable. Necessary requirement for absorption measurements of rotational transitions is the existence of a permanent dipole moment. If this doesn’t exist, but an anisotropic polarizability perpendicular to the axis of rotation, Raman scattering can be used.

Investigated are in principle only gaseous samples, so the applicability is limited. Nevertheless important parameters can be derived.

6.1.1 Experimental Setup

A scheme of the experimental setup is shown in Fig. 6.1. Generation of microwaves is done by klystrons or Gunn diodes. Low pressures of the gases are used to decrease the amount of collisions and wave guides can be up to 1 m long for higher sensitivity. Similar to ESR (Chapter 5), modulation fields are used that also give rise to the Stark effect (see chapter 6.1.4 below).
6.1.2 Quantum Mechanical Description

The moment of inertia \( I = m_r r^2 \) (for a diatomic molecule) is central to the discussion of rotational spectroscopy. The Hamilton operator can be written as

\[
\mathcal{H} \psi = -\frac{\hbar^2}{2I} \frac{\partial^2 \psi}{\partial \phi^2} = E \psi
\]  

(6.1)

with \( \phi \) being one of the spherical coordinates.

From this the differential equation

\[
\frac{\partial^2 \psi}{\partial \phi^2} = -\frac{2IE}{\hbar^2} \psi
\]  

(6.2)

The eigenfunctions can be written as

\[
\psi_J = \sqrt{\frac{1}{2\pi}} e^{iJ\phi}
\]  

(6.3)

with

\[
J = \pm \sqrt{\frac{2IE}{\hbar}} = 0, \pm 1, \pm 2
\]  

(6.4)

being the rotational quantum number.

The energy values are

\[
E = \frac{J^2 \hbar^2}{2I}
\]  

(6.5)

This derivation from classical starting points is only almost complete, \( J^2 \) has to be replaces by \( J(J + 1) \). This is because the axis of rotation was arbitrarily fixed, though many different axis perpendicular to the molecular axis are possible.
6.1. ROTATIONAL SPECTROSCOPY

We get

\[ E_J = J(J + 1) \frac{\hbar^2}{2I} = hBJ(J + 1) \]  

(6.6)

with the rotation constant \( B \) defined as

\[ B = \frac{\hbar}{4\pi I} = \frac{\hbar}{8\pi^2 I} \]  

(6.7)

given in frequency units.

The constant \( B \) becomes apparent as half of the frequency difference in rotational transitions. For this, consider the rotational transitions \( J - 1 \rightarrow J \) and \( J \rightarrow J + 1 \). For the energy differences we obtain \( \Delta E_{J,J-1} = 2hBJ \) and \( \Delta E_{J+1,J} = 2hB(J + 1) \). In frequencies, the separation is \( \frac{E}{K} = 2B \).

In the energy diagram, Fig. 6.2, it is important to note that the separation of the energy levels increases with increasing \( J \).

For rotationally symmetric non-linear molecules, we can define a symmetric tensor of inertia with characteristic values parallel to the axis of symmetry \( I_\parallel = I_z = I_A \) and perpendicular to the axis of symmetry \( I_\perp = I_x = I_y = I_B \). If \( I_A > I_B \) the rotor is shaped like a pancake, like in \( \text{C}_6\text{H}_6 \), in the opposite case, \( I_A < I_B \) like a cigar, like in \( \text{CH}_3\text{Cl} \).

The two spherical coordinates \( \theta \) and \( \phi \) describe the rotation of the molecule around arbitrary axes. The then resulting energy values are

\[ E_{\text{Rot}} = \frac{\hbar^2}{2I_B} [J(J + 1) - K^2] + \frac{\hbar^2}{2I_A} K^2 \]  

(6.8)

with \( 0 \leq K \leq J \). If \( K = 0 \) the axis of rotation is perpendicular to the molecular axis of symmetry analogous to the derivation above. With \( K = J, J \gg 1 \), the second term is dominant and the axis of rotation is almost parallel to the axis of symmetry. Selection rules are \( \Delta J = \pm 1 \) and \( \Delta K = 0 \). For Raman spectra \( \Delta J = 0, \pm 2 \).

For asymmetric rotors and also free inner molecular rotations one can give expressions with more quantum numbers, which we skip here. A question arises, if rotational spectra of spherical molecules such as \( \text{CH}_4 \), \( \text{SiH}_4 \) or \( \text{SF}_6 \) can be obtained. Though the molecules have no dipolar moment, for the tetrahedral \( \text{CH}_4 \) rotation around the \( C_3 \) axis can lead to centrifugal distortion changing three of the four \( \text{C-H} \) bond lengths and thereby creating a small dipolar moment. For example for \( \text{SiH}_4 \) at 4 bar pressure a dipole moment of \( \mu = 2.7 \cdot 10^{-35} \text{Cm} \) was determined. For comparison, \( \text{CO} \) has a dipole moment of \( \mu = 3.74 \cdot 10^{-31} \text{Cm} \). For octahedral \( \text{SF}_6 \), however
rotation around the $C_4$ axis would change the four S-F bonds in the plane but in the same way which still results in a dipole moment of 0.

### 6.1.3 Rigid and Non-Rigid Rotor

We will now explain the specifics of two examples of diatomic molecules and their effects on the rotational spectra.
• Rigid Rotor, HI Fig. 6.3 indicates the necessary symbols within the HI molecule.

![Diagram of the diatomic rotator HI](image)

**Figure 6.3: The diatomic rotator HI.**

The axis of rotation is perpendicular to the bonding axis and passes through the center of mass. The moment of inertia can be simply expressed as $I = r^2 m_r$, with $m_r$ being the reduced mass $m_r = \frac{m_1 m_2}{m_1 + m_2}$.

Experimentally, the spectrum consists of equidistant lines separated by $2B = 384$ GHz. From this we can determine the moment of inertia

$$I = m_r r_c^2 = 4.37 \cdot 10^{-47} \text{kgm}^2$$

and together with the reduced mass (mass number of 127 for iodine, only one isotope)

$$m_r = 1.65 \cdot 10^{-26} \text{kg}$$

the interatomic distance can be obtained

$$r_c = \sqrt{\frac{I}{m_r}} = 1.63 \text{Å}$$

Therefore, from the moment of inertia distances and valence angles can be obtained if the isotopic composition is known or otherwise the isotopic composition can be obtained if the interatomic distances are known. For asymmetric
molecules, three different moments of inertia can be obtained which result in a number of distances and angles. With isotopic replacement (e. g., H with D) the number of measured values can even be increased.

- Non-rigid rotor, HCl Interatomic distances can increase with increasing rotational frequency due to centrifugal distortion. For rotational spectra, this means that $B$ gets smaller with increasing $J$. Varying interatomic distance can be understood by a vibration frequency as

$$\omega_s = 2\pi
u_s = \sqrt{\frac{k}{m_r}}$$

(6.12)

with $k$ being the force constant. With that the interatomic distance can be expressed as

$$r = r_e + f_a \cos \omega_s t$$

(6.13)

With centrifugal force and displacement force being equal

$$m_r r_e \omega_{\text{rot}}^2 = k(r - r_e)$$

(6.14)

we obtain with the moment of inertia $I = m_r r^2$ and angular momentum $L = I \omega_{\text{rot}} = m_r r^2 \omega_{\text{rot}}$, the rotational energy is composed of a rigid part and an elastic part

$$E_{\text{Rot}} = \frac{L^2}{2I} - \frac{k(r - r_e)}{2}$$

(6.15)

Going from the classical to the quantum-mechanic description, with $r^3 = r_e^3$ and $L^2 \rightarrow J(J+1)\hbar^2$ the energy is

$$E_{\text{Rot}} = \frac{\hbar^2 J(J+1)}{2I} - \frac{\hbar^4 J^2(J+1)^2}{2I^2 r_e^2 k}$$

(6.16)

$$= BJ(J+1) - DJ^2(J+1)^2$$

(6.17)

where $D$ describes the elastic strain constant due to centrifugal distortion. With the relation above $D$ can be expressed as

$$D = \frac{\hbar^3}{4\pi I^3 \omega_s^2} = \frac{4B^3}{\nu_s^2}$$

(6.18)

This means that a large moment of inertia ($D \propto \frac{1}{I^3}$) and/or a large vibrational force constant ($D \propto \frac{1}{\nu_s^2}$) lead to a small distortion.

For gaseous HCl the experimentally obtained values are $2B = 20.79 \text{cm}^{-1}$ and $D = 0.00054 \text{cm}^{-1}$. 
6.1.4 Stark Effect

The Stark effect, discovered 1913 by Johannes Stark describes the lifting of the degeneration of energetic levels due to an external electrostatic field (in analogy to the Zeeman effect in external magnetic fields). In rotational spectra, there is a linear and a quadratic Stark effect where the energetic splitting of the lines is linearly or quadratic dependent on the external field strength.

For the explanation of the Stark effect, consider Fig. 6.4. We can define an effective dipole moment along the axis of rotation. The component perpendicular to this axis is average out by quick molecular rotation. With \( |\vec{K}| = K\hbar \) and \( |\vec{J}| = \sqrt{J(J+1)}\hbar \) we obtain

\[
|\vec{m}\mu_{\text{eff}}| = |\vec{m}\mu| \frac{K}{\sqrt{J(J+1)}}
\]

(6.19)

\[|\vec{m}\mu_{\text{eff}}| = |\vec{m}\mu| \frac{K}{\sqrt{J(J+1)}}
\]

(6.19)

\[|\vec{m}\mu_{\text{eff}}| = |\vec{m}\mu| \frac{K}{\sqrt{J(J+1)}}
\]

(6.19)

Figure 6.4: Orientation of \( \mu \) with respect to \( J \) and \( E \).

In the same sense, the alignment of \( \vec{J} \) with the external field depends on the magnetic quantum number \( M_J = -J, \ldots, +J \) and we can define a component \( \vec{\mu}_E \) as

\[
|\vec{\mu}_E| = |\vec{\mu}_{\text{eff}}| \frac{M_J}{\sqrt{J(J+1)}}
\]

(6.20)

For the interaction energy we obtain

\[
W_{J,K,M} = -\vec{\mu}_{\text{eff}} \vec{E} = -\mu E \frac{K M_J}{J(J+1)}
\]

(6.21)
From $W(J) - W(J-1)$ the linear Stark shift of rotational lines is

$$\Delta \nu_{\text{linear}} = \frac{\mu E}{h} \frac{2KM_J}{J(J^2 - 1)} \quad (6.22)$$

From $M_J$ we get $2J+1$-fold splitting and the dipole moment $\mu$ can be determined if $K$ and $M_J$ are known. Clearly, for linear molecules the linear Stark effect does not exist, since $K = 0$.

The quadratic Stark effect is more frequent than the linear one. External electric fields cause polarization effects so that it is also existing if there is no permanent dipole moment. For linear molecules the frequency shift is given without derivation as

$$\Delta \nu_{\text{quadratic}} = \left(\frac{\mu E}{h}\right)^2 \frac{6M_J^2(8J^2 - 3) - 8J^2(J^2 + 1)}{2BJ(J^2 - 1)(4J^2 - 1)(4J^2 - 9)} \quad (6.23)$$

### 6.1.5 Line Intensities

For the intensity of rotational lines, start with the Boltzmann distribution

$$\frac{N_i}{N} = e^{-\frac{E_i}{kT}} \sum_i e^{-\frac{E_i}{kT}} \quad (6.24)$$

The denominator contain the sum of states. With $E_J = hBJ(J + 1)$ we obtain

$$\sum_i e^{-\frac{E_i}{kT}} = \sum_J (2J + 1)e^{-\frac{E_J}{kT}} = \frac{kT}{hB} \quad (6.25)$$

On the left side of the equation the summation is both over $J$ and $M_J$ whereas on the right side only over $J$. For the Boltzmann distribution we then obtain

$$\frac{N_J}{N} = (2J + 1)\frac{hB}{kT} e^{-\frac{E_J}{kT}} \quad (6.26)$$

After differentiation with respect to $J$ and setting the result to zero we obtain for the rotational quantum number with the highest occupation (intensity)

$$J = \sqrt{\frac{kT}{2hB} - \frac{1}{2}} \quad (6.27)$$

Due to the competing effect of the exponential and the term $(2J+1)$ the maximum intensity lies at medium rotational quantum numbers, see Fig. 6.5. Due to the temperature dependence, it can also be used to determine the temperature in the absorption cell.
6.2 Vibrational Spectroscopy

6.2.1 Harmonic Oscillator

Classically, the vibration can be described similar to a spring in mechanics

\[ F = -fx \]  
\[ V = \frac{1}{2}fx^2 \]  

Quantum mechanically, we can write

\[ -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2}fx^2 \psi = E\psi \]  
\[ \Rightarrow \frac{\partial^2 \psi}{\partial y^2} + (\epsilon - y^2)\psi = 0 \]  

with the definitions

\[ y = \frac{x\sqrt{mf}}{\sqrt{\hbar}} \]  
\[ \epsilon = \frac{2E\sqrt{m}}{\hbar \sqrt{f}} = \frac{E}{\frac{1}{2}\hbar \omega} \]
For a diatomic molecule, $m$ is replaced by the reduced mass $m_r$ and $x$ denotes the deviation from the equilibrium distance $x = r - r_e$. The Schrödinger equation can be solved with $\psi = He^{-\frac{1}{2}x^2}$ which has solutions only for $\epsilon = 2v + 1$ with $v$ being integer and denoting the vibrational quantum number. The corresponding energy values are

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

(6.34)

The energy levels are equidistant, selection rule for vibronic transitions is $\Delta v = \pm 1$. A representation of the probability distribution for the different energy values is given in Fig. 6.6.

Figure 6.6: Probability density of the vibrational energy levels for the harmonic oscillator.
6.2. VIBRATIONAL SPECTROSCOPY

6.2.2 Transition moment for IR and Raman Spectroscopy

To illustrate the differences between the two modes of detection for vibrational transitions, let’s consider the transition moment:

For IR-spectroscopy, this can be defined as

\[ R_v = \int \psi_v^* \mu \psi_v'' \, dx, \quad x = r - r_e \]  

where the ’ denotes the final and ” the starting vibrational state.

Remember, that for a homonuclear diatomic molecule since \( \mu = 0 \), there is no IR detection possible. If we expand the dipole moment with respect to the equilibrium distance

\[ \mu = \mu + \left( \frac{d\mu}{dx} \right)_e x + \frac{1}{2!} \left( \frac{d^2\mu}{dx^2} \right)_e x^2 + \ldots \]  

we obtain for the transition moment

\[ R_v = \mu_e \int \psi_v^* \psi_v'' \, dx + \frac{d\mu}{dx} \int \psi_v^* x \psi_v'' \, dx + \ldots \]  

The first term is zero because all vibrational function are orthogonal to each other. Then the second term sets the selection rule \( \Delta v = \pm 1 \). For the intensity of the vibrational transition we thus obtain

\[ \text{intensity} \propto |R_v|^2 \propto \left( \frac{d\mu}{dx} \right)_e^2 \]  

For Raman spectroscopy, we have to consider the polarizability tensor \( \alpha \) which defines an ellipsoid who is expanded or contracted by vibrations due to a change in the bond length.

In a similar way as above, we can define the polarizability

\[ \alpha = \alpha_e + \left( \frac{d\alpha}{dx} \right)_e x + \frac{1}{2!} \left( \frac{d^2\alpha}{dx^2} \right)_e x^2 + \ldots \]  

and obtain for the transition moment

\[ R_v = \left( \frac{d\alpha}{dx} \right)_e A \int \psi_v^* x \psi_v'' \, dx + \ldots \]
which also results in the selection rule $\Delta v = \pm 1$. $A$ is the amplitude of the oscillating electric field. For the Raman intensity we obtain

$$\text{intensity} \propto |R_v|^2 \propto \left(\frac{d\alpha}{dx}\right)_e$$  \hspace{1cm} (6.41)

### 6.2.3 Anharmonic Oscillator

As demonstrated in Chapter 3.2, the harmonic oscillator does not represent the observed behavior for diatomic molecules, as for instance the dissociation is not considered.

A simple anharmonic potential is the Morse function

$$U_{\text{Morse}} = D_e(1 - e^{-a(r-r_e)})^2 - D_e$$  \hspace{1cm} (6.42)

with $D_e$ being the dissociation energy and $a = \sqrt{\frac{m}{2D_e}}\omega$ the vibrational angular frequency.

From the Schrödinger equation of the anharmonic oscillator we obtain the energy values

$$E_{\text{Morse}}(v) = (v + \frac{1}{2})\omega\hbar - (v + \frac{1}{2})^2\frac{(\omega\hbar)^2}{4D_e} - D_e$$  \hspace{1cm} (6.43)

A representation of the vibrational levels is given in Fig. 6.7. Note that the distance of the energy levels decreases with increasing $v$ and the difference between the chemical dissociation constant $D_0$ and the spectroscopic dissociation constant $D_e$.

A better representation than the Morse potential of the experimental findings can be obtained from a power series according to

$$\frac{E(v)}{\omega\hbar} = (v + \frac{1}{2}) - x_v(v + \frac{1}{2})^2 + y_v(v + \frac{1}{2})^3 + \ldots$$  \hspace{1cm} (6.44)

which however lacks the simple assignment of the dissociation constant.

### 6.2.4 Rotation-Vibration Spectra

In gases a rotational substructure to the vibrational transitions can be observed. For the harmonic approximation the transition frequencies are given as

$$\frac{E(v, J)}{\hbar} = (v + \frac{1}{2})\nu + BJ(J + 1)$$  \hspace{1cm} (6.45)
6.2. VIBRATIONAL SPECTROSCOPY

Figure 6.7: Vibrational energy levels for the anharmonic oscillator.

with assuming \( B \) is constant we obtain for the transition between the vibrational ground state labeled \( \nu \) and the vibrational excited state labeled \( \nu' \) with the selection rules \( \Delta \nu = 1 \) and \( \Delta J = 0 \)

\[
\frac{\Delta E}{\hbar} = \frac{E(\nu', J')}{\hbar} - \frac{E(\nu'', J'')}{\hbar} = v + Bm
\]  

(6.46)

with \( m = 0 \) if \( \Delta J = 0 \) and \( m \) positive if \( \Delta J = +1 \) and negative if \( \Delta J = -1 \).

As an example consider the example of HCl in Fig. 6.8. For \( m \) being negative this is referred to as the P-branch and for positive values the R-branch. For \( m = 0 \) it is called Q-branch. For this, a non-zero moment of inertia for rotation around the interatomic axis is necessary, which for diatomic molecules is only observed in paramagnetic NO.

The energy separations for the different branches are obtained as

\[
\frac{\Delta E}{\hbar} = v + (B' + B'')(J'' + 1) + (B' - B'')(J'' + 1)^2 \quad \text{R - branch} \tag{6.47}
\]

\[
\frac{\Delta E}{\hbar} = v + (B' - B'')(J'' + (B' - B'')J''^2 \quad \text{Q - branch} \tag{6.48}
\]

\[
\frac{\Delta E}{\hbar} = v + (B' + B'')(J'' + (B' - B'')J''^2 \quad \text{P - branch} \tag{6.49}
\]
For the P-branch the lowest values for \( J'' \) is 1, whereas for the R- and Q-branch it is 0.

For multiatomic molecules, rotation-vibration spectra are more complicated and categorized by the type of rotor (see chapter 6.1. Also further selection rules exist taking into account if the dipole moment of the vibrational transition is parallel or perpendicular to the axis of the top through the center of mass.

### 6.2.5 Experimental Setup

For IR experiments, cw and FT spectrometers have to be differentiated. In cw-IR, a light source transmits through the sample and by beam splitting also through a reference cell. An adjacent monochromator before the detector allows for frequency dependent detection of the adsorption.

In FT-IR, the light passes through the sample onto a partially transmittable mirror. One part leads to the detector, the other part is reflected from a movable mirror. Nowadays, new IR-spectrometers are all FT-IR spectrometers.

All kinds of sample can be investigated. Gases, liquids and solutions of samples in a solvent are put in glass containers usually made from NaCl that doesn’t show absorption in the IR range. For solids, two methods are possible, either a suspension in an oil such as Nujol or the preparation of a KBr plate under pressure. Small amounts of solid are included. Otherwise absorption of IR light would be too high. Another possibility is to use attenuated total reflection (ATR) from a solid surface.
For Raman spectroscopy, a monochromatic light source is needed. In former days this complicated the use of Raman spectroscopy, but with the nowadays available lasers (see chapter 7.5) Raman spectroscopy is more and more used. The light is scattered on the sample and the scattered light detected with lenses or mirrors in a similar way to FT-IR.

A schematic overview of the different spectrometer types is shown in Fig. 6.9.

Whereas IR spectroscopy is well suited for polar bonds such as O-H, Raman spectroscopy is more sensitive for non-polar bonds such as C=C, N=N, C-C, O-O. Weak bands are observed for instance for C=0 or C-H bonds. Another advantage is that water can be used as solvent which would produce a huge absorption peak in the IR.
6.2.6 Polyatomic Molecules

For polyatomic molecules there are $3N-5$ or $3N-6$ vibrations for linear/non-linear molecules. Not all of these vibrations need to be observable (see chapter 3.4). A classification of different types of vibrations is given in Fig. 6.10.

Due to the multiple vibrations, calculation of IR (or Raman) spectra is quite complicated, if not impossible. For that, databases are created that contain spectra of a large number of molecules. The complication also comes into play by the presence of so-called coupled vibrations, i.e., the displacement of one nucleus leads to a complicated motion of the other nuclei that are bonded to it leading to a mixture of angle-bending and bond-stretching motions.

Nevertheless, there can be a classification of two regions of the IR spectrum for at least organic molecules. For wavenumbers above 1500 cm$^{-1}$ we speak of localized vibrations and below 1500 of backbone vibrations. The latter are characteristic for the molecule as an entity and is therefore also called 'fingerprint' area. Localized vibrations are useful for the identification of functional groups. This is rather easy.
to understand for terminal groups such as the hydroxyl group $\text{-O-H}$ which has a very strong absorption band at $3600\text{ cm}^{-1}$. Because of the classical relation $\omega = \sqrt{\frac{k}{m}}$, we can also conclude that

- a higher atomic mass leads to smaller wavenumbers: $\text{C-H bond } \approx 3000\text{ cm}^{-1}$
  
  $\text{C-D bond } \approx 2100\text{ cm}^{-1}$

- a larger force constant leads to larger wavenumbers: $\text{C} \equiv \text{C } 2200\text{ cm}^{-1}$
  
  $\text{C}=\text{C } 1640\text{ cm}^{-1}$

  $\text{C-C } 1000\text{ cm}^{-1}$

For heavier atoms or in transition metal complexes, clearly localized vibrations move to the 'fingerprint' area.

6.3 References

general:


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Chapter 7

UV-VIS Spectroscopy

Transitions of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) usually require electromagnetic radiation in the nanometer wavelength which is visible or ultraviolet light.

Because of this wavelength range it belongs to the oldest spectroscopies (see chapter 1). A classification of wavelengths and colors can be given as

- $\lambda > 780\, nm$: IR
- $\lambda = 700\, nm$: red
- $\lambda = 620\, nm$: orange
- $\lambda = 580\, nm$: yellow
- $\lambda = 530\, nm$: green
- $\lambda = 470\, nm$: blue
- $\lambda = 420\, nm$: violet
- $\lambda < 380\, nm$: UV
- $\lambda < 300\, nm$: quartz-UV
- $\lambda < 150\, nm$: vacuum-UV
It should be stressed here, that the classification and nomenclature of colors differs for different countries and additionally that personal recognition of color differs for different people.

The process of vision is realized by the molecules 11-cis-retinal which upon absorption of a photon is reacting to the all-trans retinal that induces a cascade of reactions in the eye and the nervous system. The absorption is characterized as a $\pi \rightarrow \pi^*$ transition, see explanation below. By variation of the surrounding protein different wavelength absorptions are possible that enable the differentiation of colors, see Fig. 7.1.

![Absorption sensitivities of S (short wavelength), M (medium), and L (long) cones.](image)

**Figure 7.1:** Absorption sensitivities of S (short wavelength), M (medium), and L (long) cones.

### 7.1 Atomic Spectroscopy

Atomic spectroscopy was dealt with already in chapters 1 and 3.3 that dealt with the spectra of atomic hydrogen (Balmer-, Paschen-, Pfund-series...) and the term symbol for polyelectronic systems.
For the Hamilton operator we can formulate
\[ \mathcal{H} = \frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r_{ij}} \] (7.1)

For polyelectronic systems this is modified to
\[ \mathcal{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \] (7.2)

Here, the first term denotes the electron motion, the second the coulomb interaction to the nuclei, and the last the electron-electron repulsion.

As this is not analytically solvable, a simplification by Hartree is done as
\[ \mathcal{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_i V(r_i) \] (7.3)

where a potential is defined as a sum of the contributions of all individual electrons.

Finally, we observe the energy levels for the different orbitals as shown in Fig. 3.8. Filling of the atomic orbitals is done using the Pauli principle and Hund’s rules. Of importance are peculiarities for orbitals of similar energy such as 3d and 4s. For stability reasons (e.g., half-filled shells) the electronic configurations of Cu is 3d\(^{10}\)4s\(^1\) whereas for Cr it is 3d\(^5\)4s\(^2\).

The following selection rules exist:

- \( \Delta n \) unrestricted
- \( \Delta l = \pm 1 \)
- \( \Delta J = 0, \pm 1 \), except for \( J = 0 \rightarrow J = 0 \)

Consider, for example the generation of the Na D-line. The ground state is a \( ^3S_{\frac{1}{2}} \) (\( l=0, s=\frac{1}{2} \)). The two lowest lying excited states are \( ^3P_{\frac{1}{2}} \) and \( ^3P_{\frac{3}{2}} \) (\( l=1, \) consider \( l+s \) or \( l-s \)). Therefore we can two transitions that are responsible for the Na D-line.

Four multi-electron systems, one has to keep in mind LS or jj-coupling (see chapter 3). If spin-orbit coupling is small, one can make the following separation of the electronic wave function
\[ \psi_e = \psi_e^{\text{orbital}} \ast \psi_e^{\text{spin}} \] (7.4)

which have the selection rules \( \Delta l = \pm 1 \) and \( \Delta S = 0 \). For atoms with large nuclear charge, however, this separation is no longer possible and therefore the spin can also change during the transition.
7.2 (Diatomic) Molecules

For molecules, recall the generation of molecular orbital by linear combination of atomic orbitals (LCAO-MO), chapter 3.2. As seen in Fig. 3.7 molecular orbital energies usually increase in the order $\sigma, \pi, n, \pi^*, \sigma^*$. Therefore, $\sigma \rightarrow \sigma^*$ transitions require more energy and therefore shorter wavelengths (often in vacuum-UV) than $\pi \rightarrow \pi^*$ transitions in the UV. Conjugation of C=C double bonds reduces the energy difference between $\pi$ and $\pi^*$ and therefore the absorption shifts to the visible range, as evident from the retinal molecule responsible for human vision.

The selection rules given for atomic spectra are slightly modified for molecules. The selection rules can be summarized as follows.

- Spin conservation, $\Delta S = 0$ (with the exception of large spin-orbit coupling)
- $\Delta L = 0, \pm 1$, except $L = 0 \rightarrow L = 0$
- $\Delta J = 0, \pm 1$, except $J = 0 \rightarrow J = 0$
- For irreducible representations transitions between even and even types and between odd and odd types are forbidden, only transition from even to odd are allowed
- In the same sense, transitions from + to + and - to - states are allowed, while from + to - are forbidden

Referring to the symmetry considerations discussed in chapter 3.4, we will consider two examples, ketones and ethylene, to illustrate observed intensities in UV/VIS spectra.

Example 1: $n \rightarrow \pi^*$ transition in carbonyl bonds

The ground state can be expressed as $\sigma^2\pi^2n^2$. Excitation leads to $\sigma^2\pi^2n^1\pi^1$. We can assign the orbitals to the different irreducible representations for the symmetry group $C_{2v}$. The $\pi$ and $\pi^*$ orbitals belong to the symmetry type $B_1$, while the $n$ orbital belongs to symmetry type $B_2$. The ground state with all orbitals filled the symmetry type is $A_1$. For the excited state we get $A_1 \times A_1 \times B_2 \times B_1 \equiv A_2$. For the transition dipole moment we have to combine the two symmetry type with that of a translation. For an allowed transition the result of the multiplication has to be the symmetry type $A_1$. This requires $A_2$ to contain a component of translation. In the
7.3. FRANCK-CONDON PRINCIPLE

symmetry group $C_{2v}$, however, this is not existing. Therefore $n \rightarrow \pi^*$ transitions in carbonyl groups are forbidden. In practice, vibrations can create for short periods of time a different symmetry where a transition is allowed. Therefore extinction coefficients of 1 to $2 \, m^2mol^{-1}$ are obtained. Due to the low extinction these are referred to as forbidden transitions (see example 2).

Example 2: $\pi \rightarrow \pi^*$ transition in ethylene

For the ethylene bond the symmetry group $D_{2h}$ is responsible. The $\pi$ orbital belongs to the symmetry type $B_{3u}$ whereas the $\pi^*$ orbital to the symmetry type $B_{2g}$. To obtain the total symmetric type, a translation with the symmetry type $B_{1u}$ is required. This is fulfilled for $z$-translation so that a $\pi \rightarrow \pi^*$ transition is an allowed transition with extinction coefficients of $1700 \, m^2mol^{-1}$.

7.3 Franck-Condon Principle

The process of electronic transitions and the observed vibrational structure was explained semi-classically by James Franck and later by Edward Uhler Condon quantum-mechanically. In the general case, the excited electronic state has a larger equilibrium distance due to anti-bonding orbitals, see Fig. 7.2. Nevertheless there can also be cases where the equilibrium distance of the excited state is smaller or equal than the state from where the excitation starts, which don’t have to be ground states.

For the explanation we can assume that electronic transitions happen quickly so that the nuclei cannot react immediately (Born-Oppenheimer approximation), so that the nuclei distance stays constant during excitation. This means a vertical process in the energy diagram. For the quantum-mechanical verification we start with the transition dipole moment for an excitation from level 1 to level 2:

$$\vec{M}_{21} = q \int \psi_2^* \vec{r} \psi_1 \, d\tau$$  \hspace{1cm} (7.5)

Neglecting rotational levels, the wave function can be split into contributions from vibrational and electronic states

$$\psi_1 = \psi_{1v} \psi_{1e}$$  \hspace{1cm} (7.6)
$$\psi_2 = \psi_{2v} \psi_{2e}$$  \hspace{1cm} (7.7)
CHAPTER 7. UV-VIS SPECTROSCOPY

Figure 7.2: Electronic transition and concomittant vibrational wave function overlap.

Together with the operator representation \( \vec{\hat{r}} = \vec{\hat{r}}_v + \vec{\hat{r}}_e \) we obtain

\[
M_{21} = q \int \psi_2^* (v, e) \vec{\hat{r}} \psi_1 (v, e) \, dv \, de (7.8)
\]

\[
= q \int \psi_2^* (v) \psi_2^* (e) [\vec{\hat{r}} (v) + \vec{\hat{r}} (e)] \psi_1 (v) \psi_1 (e) \, dv \, de (7.9)
\]

\[
= q \int \psi_2^* (v) \psi_1 (v) \, dv \int \psi_2^* (e) \psi_1 (e) \, de (7.10)
\]
7.4. LUMINESCENCE, FLUORESCENCE, AND PHOSPHORESCENCE

Table 7.1: Definitions for fluorescence and phosphorescence.

<table>
<thead>
<tr>
<th></th>
<th>fluorescence</th>
<th>phosphorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>time of existence</td>
<td>&lt; $10^{-8}$s</td>
<td>$&gt; 10^{-8}$s</td>
</tr>
<tr>
<td>molecular process</td>
<td>monomolecular</td>
<td>biomolecular</td>
</tr>
<tr>
<td>dying out of intensity</td>
<td>exponential</td>
<td>hyperbolic</td>
</tr>
</tbody>
</table>

$$+q \int \psi_2^*(v) \bar{r}(v) \psi_1(v) d\tau(v) \int \psi_2^*(e) \psi_1(e) d\tau(e)$$  \hspace{1cm} (7.11)

The second term is zero since the wave functions of the electronic states are all orthogonal to each other (by definition). This is not true for the vibrational states in the first term since the vibrational states belong to different sets of wave functions, the two different electronic states. Therefore the pre-factor $\int \psi_2^*(v) \psi_1(v) d\tau(v)$ or better the square of it represents the overlap of the vibrational wave functions between ground and excited electronic state. This means, referring to Fig. 7.2 that an excitation from the electronic and vibrational ground state is most probable into a higher vibrational state of the excited electronic state.

7.4 Luminescence, Fluorescence, and Phosphorescence

In general, luminescence describes the emission of light after absorption. This is to differentiate it from thermal radiation as for instance black body radiation. Different types of radiation are distinguished depending on the way absorption is taking place, such as photoluminescence, electroluminescence or chemoluminescence among others.

From historical reasons, fluorescence and phosphorescence are differentiated, however, there are different definitions existing as shown in Table 7.1.

Unfortunately, these criteria are not always fulfilled for differentiation. An explanation of the two phenomena can be given according to the energy diagram in Fig. 7.3 which is also known as Jablonski term scheme.

Fluorescence then describes the emission from an excited electronic singlet to
the singlet ground state while phosphorescence is emitted light coming from an triplet state which requires spin change. Additionally, radiationless processes exist where energy can be given to the lattice without emission which is known as internal conversion (IC). This is also responsible for the fact that fluorescence usually has a longer wavelength than the absorbed light. For the change of spin state from singlet to triplet or vice versa these radiationless processes are named intersystem crossing (ISC).

### 7.5 LASER

LASER is principally the abbreviation for Laser Amplification by Stimulated Emission of Radiation. Due to the many applications and the daily use of the word, the word 'laser' is now also frequently used.

Characteristic for a laser is the monochromatic, coherent light with high radiant power. Monochromatic here means that the line width is extremely small (see also dye lasers below).

#### 7.5.1 Operating Conditions

The first requirement for a laser is that the probability for induced emission is higher than for absorption. If we refer to Fig. 2.2 this requires that \( N_2B_{21}w_0 > N_1B_{12}w_0 \)
7.5. LASER

(disregarding degeneracy of energy levels). Since $B_{12} = B_{21}$, we get to the first lasing condition

$$N_2 > N_1$$ (7.12)

From Boltzmann statistics we know that $N_2 < N_1$, so we need a way to create population inversion.

This can be achieved, e.g., by oscillation excitation. Here, we have an active medium (see description for different lasers below) that absorbs a photon into an excited state. Excitation leads to the fact that a high amount of atoms or molecules are in the excited state. The active medium is within a resonator with fixed length $L$ between two mirrors. By stimulated emission the number of photons increases. If the emitted wavelength follows

$$L = \frac{\lambda}{2} \Leftrightarrow \nu = q \frac{c}{2L}$$ (7.13)

we get constructive interference and the intensity increases. One of the two mirrors is not a perfect mirror (reflectivity $< 100\%$, so that there is a chance for the laser light to escape and produce highly oriented, monochromatic laser light.

If we set for the intensity change

$$dI = \sigma I (N_1 - N_2) dz = -\alpha I dz$$ (7.14)

(I: photon number flux density, $\sigma$ interaction cross section and $\alpha = (N_2 - N_1)\sigma$ frequency dependent absorption coefficient)

With that the intensity gain can be expressed after one back and forth reflection as

$$G(2L) = \frac{I(2L)}{I(0)} = e^{-2\alpha L}$$ (7.15)

The non-perfect reflectivity of the two mirrors can be taken into account by a term $\gamma$ so that

$$G(2L) = \frac{I(2L)}{I(0)} = e^{-2\alpha L - \gamma}$$ (7.16)

which leads to a threshold value, the second lasing condition

$$\Delta N = N_2 - N_1 > \Delta N_{\text{threshold}} = \gamma(2\sigma L)$$ (7.17)

One method to create population inversion is known as optical pumping, see Fig. 7.4.
Excitation goes from the ground state (or any laser level 1) to an excited state level 3 from which it rapidly falls back on laser level 2 via non-radiative processes. From laser level 2 the laser emission proceed which competes with a non-radiative process. The transition rates for the non-radiative processes are denoted as $T_{32}^{-1}$ and $T_{21}^{-1}$.

With the pumping rate $P = \sigma_{13} I_p$, and $N_3 \approx PT_{32}N_1 \ll N_1, N_2$, we can define for the changes in population

$$\frac{dN_2}{dt} = -\sigma_{12} I_L (N_2 - N_1) - \frac{N_2}{T_{21}} + PN_1$$  \hspace{1cm} (7.18)$$

$$\frac{dN_1}{dt} = +\sigma_{12} I_L (N_2 - N_1) + \frac{N_2}{T_{21}} - PN_1$$ \hspace{1cm} (7.19)$$

With the definitions $\Delta N = N_2 - N_1$ and $N = N_1 + N_2$ we obtain

$$\frac{d\Delta N}{dt} = -2\sigma_{12} I_L \Delta N \left( P + \frac{1}{T_{21}} \right) \Delta N + \left( P - \frac{1}{T_{21}} \right) N$$ \hspace{1cm} (7.20)$$

In a stationary condition ($\frac{d\Delta N}{dt} = 0$), we get

$$\Delta N_{\text{stationary}} = \frac{\left( P - \frac{1}{T_{21}} \right) N}{\left( P + \frac{1}{T_{21}} \right) + 2\sigma_{12} I_L}$$ \hspace{1cm} (7.21)$$
For the requirement of positive $\Delta N_{\text{stationary}}$, we get

$$P_{\text{critical}} = \frac{1}{T_{21}} \quad (7.22)$$

This requires that the non-radiative process from level 2 to 1 has to be slow.

### 7.5.2 Types of Lasers

Lasers are subdivided according to the materials that are used. Here, a few examples will be given.

- Nd-YAG solid-state laser Yttrium aluminum garnet doped with about 1% neodymium is used where the Nd$^{3+}$ ground state is $^{4}I_{9/2}$. Due to the YAG crystal field transitions from the excited states $^{4}F_{5/2}$ and $^{4}F_{7/2}$. Pumping wavelengths is 808 nm and laser emission is 1064 nm which can be changed to 532 nm by frequency doubling. This is an example of the four-state laser, see Fig. 7.5 to illustrate the energy levels.

![Energy diagram for the Nd:YAG laser.](image)
- Ruby laser: The ruby laser represents the first realized laser, created 1960 by Theodore Maiman. Ruby is corundum, $\text{Al}_2\text{O}_3$ doped with 0.1 \% $\text{Cr}^{3+}$. It is a three-level laser with the ground state being $^4A_2$, the pumping levels $^4F_2$ or $^4F_1$ and the upper laser level being a $^2E$ state. This means, that change from a quartet to a doublet state and vice versa has to occur. The laser wavelength is 694 nm.

- HeNe laser: Helium and neon are mixed in a ratio of 5 to 1. Excitation is done on the helium atom which transfers energy to neon atoms through collisions. Three laser transitions with wavelengths of 3.39 $\mu$m, 1.15 $\mu$m and 633 nm are generated. The more complicated energy diagram is shown in Fig. 7.6.

- Argon laser: Excitation is realized through electron collisions from the atom to an ionic ground state to the pumping level. About 20 transitions in the range 450 to 530 nm occur due to L and J splittings.
7.5. LASER

• CO₂ laser Additional to CO₂ N₂ and He (among others) are present in the gas chamber to prevent chemical reactions. By electric excitation a metastable N₂ level is generated and molecular collisions transfer the energy to CO₂. Two laser levels with 9.6 and 10.6 µm wavelength in the IR correspond to the symmetric valence vibration and a bending vibration. The energy diagram is shown in Fig. 7.7.

![Energy diagram for the CO₂ laser.](image)

• semiconductor laser p- and n-doped semiconductors are electrically driven to achieve polarization inversion and an electron-hole combination happens. For different semiconductors wavelengths in the range 400 nm to 4 µm are possible. The GaAs laser for instance leads to 850 nm light. Instead of mirrors, often the crystal boundaries are sufficient.

• dye laser Here dye molecules are dissolved in a solvent such as ethanol, methanol or water which are often used in flow mode to prevent bleaching of the dye molecules. The fluorescence from an excited state S₁ to the ground state S₀ is used. Due to rotation-vibrations broader wavelength ranges are obtained, typically of 50 nm. Dye lasers are often pumped by other lasers. A lower efficiency is usually observed compared to other lasers but the high number of dye molecules easily enables the generation of lasers with strongly different wavelengths.
Nowadays, there are also tunable lasers, like the Ti-Sapphire laser existing, that will not be covered here.

7.6 References

general:


M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der organischen Chemie, Georg Thieme.