Theoretical Physics II

Quantum Mechanics

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Chapter 1

Introduction

1.1 Developing theories in natural sciences and the significance of quantum mechanics

Quantum mechanics, together with the theory of relativity, represents one of the two *great revolutions* in physics marking the beginning of "modern physics", in contrast to the period of classical physics of the 19th century and the time before. Both theories form the basis of today's understanding of nature: The theory of relativity, in general, with its only relevance under extreme conditions (high velocities, huge masses, cosmology, particle collider) and quantum mechanics, which determines numerous phenomena of our daily environment. One important example of relativity, even at everyday available energy levels, is the magnetic spin, which can only be understood by means of quantum mechanics in combination with relativity.
Until the end of the 19th century the world view of natural sciences was based on (Newton's) classical mechanics and (Maxwell's) electrodynamics; that is: It was *mechanistic, deterministic*. However, unsolved problems existed:

- What is the source of the sun's energy?
- Why are atoms solid? (Radiation decay)
- Why does hot atomic gas have a discrete spectrum?

At first, one didn't consider these problems as urgent and expected them to be

solved soon within the theory of classical physics. From what we know today, this was a fallacy. Only by *remodeling* the physical theory completely, understanding could be achieved. At the beginning of the 20th century, new improved experiments developed, pushing towards a solution of these unsolved problems and proved not only that these experiments were difficult to understand within the theory of classical physics, but that their explanation was inconsistent with classical physics. Some of these mostly in *microcosm* tested experiments were:

- Spectroscopy of atoms
- Scattering experiments between particles (electron) and light (photon): Compton-effect, photoelectric effect
- Interference of light-/particle radiation: Double slit experiment

These and other experiments demonstrated, that on the level of elementary particles (where the scale yet has to be defined), these small elements behaved like *waves* as well as *particles* (wave-particle-dualism). Furthermore, some physical quantities proved to be only of *quantized* values and causality was given only by its mean. Astonishingly, within *20 years* the works of only *a few* people (Planck, Einstein, Heisenberg, Schrödinger, Dirac, Pauli, Born) let to a complete new theory, the Quantum Theory, which allowed correct specifications of these microscopic phenomena from then on. Therefore, we refer to this development as a *revolution*.

From this example we can now derive (see figure 1.3), how a physical theory arises in general.

One observes four substantial properties of the process of discovery:

1. Once experiments reach so far unknown territory, results are difficult to understand and tend to be misinterpreted.

   Reason: In the process of evolution our brains adjusted to everyday life (antropic principle); Phenomena out of human's experiential range of knowledge remain inaccessible.

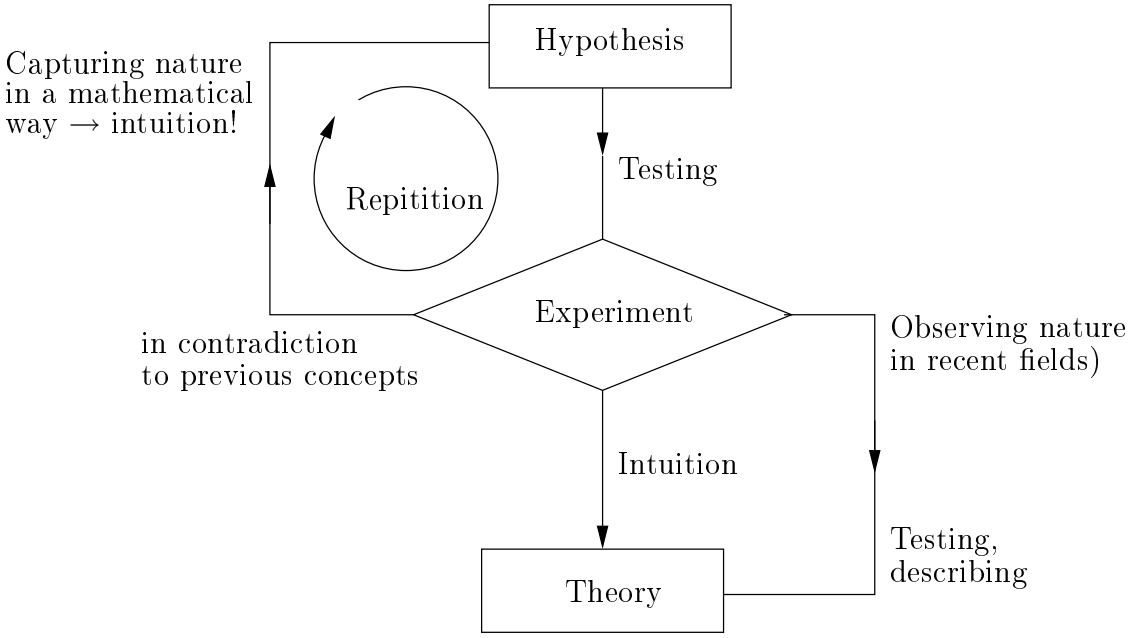

Figure 1.1: Development of a theory

2. Concerning the description of new phenomena, mathematics is an essential complementary science.

3. In contrast to mathematics, mapping nature onto mathematical formalism is never rigorous, but always requires *intuition*. On the other hand, the *interpretation* of a mathematical theory's results in order to describe nature asks for adjustment.

4. A theory has to be tested continuously by comparing it to the experimental results.

Particularly point three can be understood in terms of the quantum mechanical evolution:

- The fundamental equation of motion of quantum mechanics (Schrödinger equation) can not be derived from other theories, for its experiential sphere goes beyond the previous boundaries. Merely, its plausibility is only derived from intuition.

- The interpretation of results and predictions asks for adjustment; "Kopenhagener prediction" (took decades). This process of discovery and revolu-

tion is undergone by the student, while studying the Quantum Theory, as well.

- Studying the mathematical formalism
- Only by adjustment and intuition understanding is possible.

1.2 Historical fundamental experiments and consequences

The basic principles of classical physics are Newton's mechanics and Maxwell's electrodynamics, describing matter as particles and electromagnetic fields as waves:

- **Classical mechanics**: Movement of matter

  Particles = Idealized point-shaped accumulation of mass m at position $\underline{\vec{x}}$ and of momentum $\underline{\vec{p}}$.

  Equation of motion:

$$m\ddot{\vec{x}} = \vec{F} = -\vec{\nabla}V(\vec{x}) \qquad \text{Newton, Euler-Lagrange} \tag{1.1}$$

$$\left.\begin{aligned} \frac{d\vec{x}}{dt} &= \frac{\partial H}{\partial \vec{p}} \\ -\frac{d\vec{p}}{dt} &= \frac{\partial H}{\partial \vec{x}} \end{aligned}\right\} \quad \text{Hamiltonian} \tag{1.2}$$

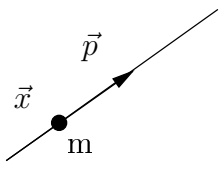

Figure 1.2: Quantities describing a single particle

- **Classical electrodynamics**: Dynamics of electromagnetic fields

  Light = wave (spatial, time extended disturbance)

  Wave-equation of frequency ω and wavelength λ :

$$\frac{1}{c}\frac{\partial^2}{\partial t^2}\,\vec{E}(\vec{x},t) - \vec{\nabla}^2\vec{E}(\vec{x},t) = 0 \tag{1.3}$$

$$\vec{E}(\vec{x},t) = \vec{E}_0\, e^{i(\vec{k}\vec{x}-\omega t)} \tag{1.4}$$

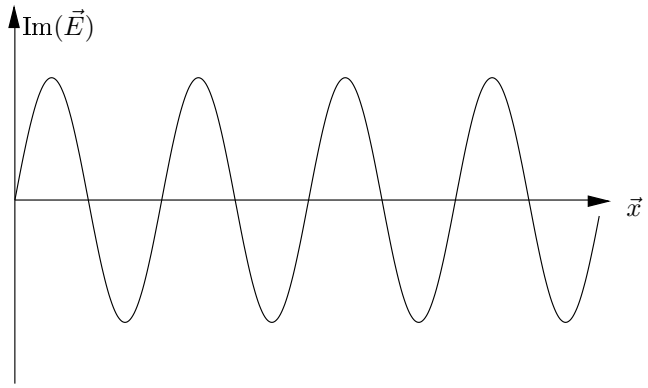

Figure 1.3: Visualization of a propagating wave

In this section we will discuss the key experiments, which let at the beginning of the 20th century to the realization, that previous ideas lost its validity once atomic quantities are reached. In the following section, we will note in each case the key ideas that contributed to the establishment of the Quantum Theory. Historically, the property of light, to show wave and particle characteristics at the same time, was detected first. Only after a while the wave characteristic of matter under certain circumstances was observed as well.

1.2.1 The photoelectric effect

Figure 1.4 shows the radiation of light on a metal surface.

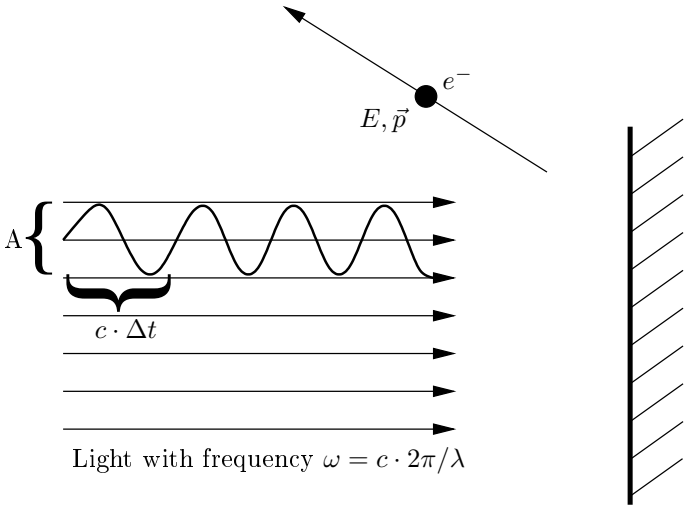

Figure 1.4: The photoelectric effect

- **Expectations according to classical electrodynamics and mechanics**:

  The energy density of the electromagnetic wave is independent of ω

  $$\frac{1}{8\pi}(E^2 + H^2) \sim I \propto \text{intensity} \tag{1.5}$$

  The energy is *continuously* transmitted onto the electrons in the metal

  $\Rightarrow$ For *arbitrarily* small frequencies the work W_a is transmitted after the time sequence Δt , that is for each electron:

  $$W_a = (c\,\Delta t) \cdot A \cdot W, \quad A = \text{Efficiency of energy transmission} \tag{1.6}$$

- **Experimental findings, as shown in figure 1.5**:

  1. Electrons are released only when the frequency of light ω exceeds the threshold value $\omega_{\min}$.

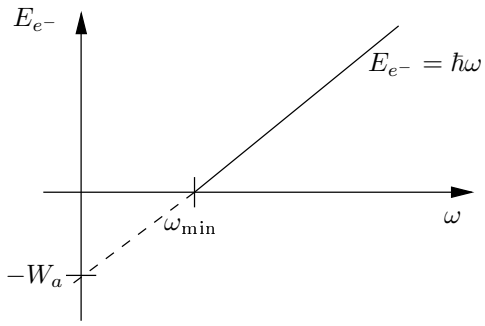

Figure 1.5: Transmitted energy

2. Electrons are released *immediately*, if $\omega > \omega_{\min}$ (not after a time Δt)
3. Their energy is given by $E_{e^-} = \hbar\omega + W_a$, while the proportional constant $\hbar$ was determined numerically as the so called "Planck constant" (Planck, 1900; Cavity radiation):

$$\boxed{\hbar = 1,055 \cdot 10^{-34} Js} \tag{1.7}$$

4. The number of released electrons per time unit (not the energy of *one* electron) is proportional to the intensity of light.

The wave property of light, the wavelength λ and frequency $\omega = c\,\frac{2\pi}{\lambda}$, as well as the particle character of electrons, the energy $E_{e^-} = \frac{p^2}{2m}$ and momentum p could be determined experimentally. Moreover, a direct relation between E_{e^-} and ω could be established.

Einstein's Interpretation (1905) (Nobel price 1921)

1. *Particle hypothesis and energy-frequency relation*

   The energy of light is transferred *directly* in packages of energy proportional to the frequency, such that:

$$\boxed{E_{\text{ph}} = \hbar\omega \quad \text{(photons)}} \tag{1.8}$$

   The threshold frequency $\omega_{\min}$ corresponds to the work function:

$$W_{\text{a}} = \hbar\omega_{\min} \tag{1.9}$$

This direct transmission and the constant energy at stationary frequency are characteristic of particles.
Einstein was the first to define these energy packages as particles and called them "photons" (a revolutionary step, Planck did not dare to take). If Einstein's particle hypothesis was true the proportional constant between energy and frequency had to be equal to the Planck constant $\hbar$, which related Planck's energy-quantums of light to the frequency. This equivalence was confirmed numerically.

2. *Momentum-wavelength relation*

While the energy-frequency relation was derived directly from the quantities E_{e^-} and ω , the relation between momentum and wavelength λ (wave number k, respectively) was established numerically, since the momentum of the photo effect is not accessible experimentally:

As particles of light, photons have to move at light-velocity $v = c$ and their mass at rest vanishes $m_{ph} = 0$. With the relativistic energy-momentum relation we obtain:

$$\begin{aligned} E &= \sqrt{m_{ph}^2 c^4 + p^2 v^2} = p\,c && (1.10)\\ &\quad \text{for} \quad m_{ph} = 0,\ v = c \quad \text{(particles)} \\ &= \hbar\,\omega = \hbar\,ck = \hbar\,c\,\frac{2\pi}{\lambda} \quad \text{(wave)} && (1.11)\\ \Leftrightarrow\ & p = \hbar\,k = \frac{2\pi}{\lambda}\hbar \quad \text{(photons)} && (1.12) \end{aligned}$$

Mathematical supplementation 1: Fourier transformation

Representation of vectors in orthonormal basis

- In general:

$$\mathbb{B} = \{|n\rangle |\, n\,\epsilon M\} \qquad \text{basis of space } \mathbb{V} \tag{1.13}$$

Arbitrary vector of $\mathbb{V}$:

$$|a\rangle = \sum_{n\epsilon M} a_n |n\rangle \quad \text{(completeness)} \tag{1.14}$$

Scalar product:

$$\langle b \,|\, a \rangle \tag{1.15}$$

$\mathbb{B}$ is orthonormal basis:

$$\langle m \,|\, n \rangle = \delta_{mn} \quad \forall\, n, m \,\epsilon M \tag{1.16}$$

Coefficients of orthonormal basis representation:

$$\langle m \,|\, a \rangle = \sum_{n \epsilon M} a_n \underbrace{\langle m \,|\, n \rangle}_{\delta_{mn}} = a_m \tag{1.17}$$

$$a_n = \langle n \,|\, a \rangle \tag{1.18}$$

$$|a\rangle = \sum_{n \epsilon M} |n\rangle \langle n \,|\, a \rangle \tag{1.19}$$

- **Specifically:** $\mathbb{V}$ space of infinite differential square-integrable functions

Basis:

$$\mathbb{B} = \{ |k\rangle = \frac{1}{\sqrt{2\pi}}\, e^{ikx} |\, k \,\epsilon \mathbb{R} \} \tag{1.20}$$

Arbitrary function of $\mathbb{V}$:

$$f(x) = \int \frac{dk}{\sqrt{2\pi}}\, f(k)\, e^{ikx} \tag{1.21}$$

Scalar product of $\mathbb{V}$:

$$\langle g \,|\, f \rangle := \int dx\, g^*(x) f(x) \in \mathbb{C} \tag{1.22}$$

$\mathbb{B}$ is orthonormal basis:

$$\langle k' |\, k \rangle = \int \frac{dx}{2\pi}\, e^{-i(k'-k)x} = \delta(k'-k) \qquad \text{(orthogonal)} \tag{1.23}$$

Coefficients of orthonormal representation:

$$f(k) = \langle k \,|\, f \rangle = \int \frac{dx}{\sqrt{2\pi}}\, e^{-ikx} f(x) \tag{1.24}$$

(1.21) and (1.24) form the Fourier transformation!

Mathematical supplementation 2: Group velocity

Velocity of wave packets ("wave group") (see figure 1.6).

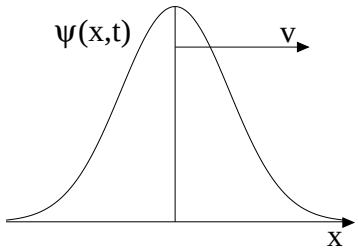

Figure 1.6: Velocity of a wave packet

Fourier representation of wave packets (superposition of plane waves):

$$\psi(x,t) = \int \frac{dk}{\sqrt{2\pi}}\, \psi(k)\, e^{i(kx-\omega_k t)} \tag{1.25}$$

To each wave number k corresponds the frequency ω_k (in general, function of k or vice versa)

Example: Wave of light in a particular medium

Expectation value of the wave packet's state in space:

$$\begin{aligned}
\bar{x}(t) &= \int dx\, x|\, \psi(x,t)|^2 && (1.26)\\
&= \int dx \int \frac{dk'}{\sqrt{2\pi}} \int \frac{dk}{\sqrt{2\pi}}\, e^{-i(k'x-\omega_{k'}t)} \psi^*(k')\, x\, \psi(k)\, e^{i(kx-\omega_k t)} && (1.27)\\
&= \int dx \int \frac{dk'}{\sqrt{2\pi}} \int \frac{dk}{\sqrt{2\pi}}\, e^{-i(k'x-\omega_{k'}t)} \psi^*(k')\, \psi(k) \left[\frac{1}{i}\frac{\partial}{\partial k} + \frac{\partial \omega_k}{\partial k} t\right] && (1.28)\\
&\quad \times e^{i(kx-\omega_k t)} &&\\
&= \int dk' \int dk\, \delta(k'-k)\, \psi^*(k')\, \psi(k) \left[\frac{1}{i}\frac{\partial}{\partial k} + \frac{\partial \omega_k}{\partial k} t\right] e^{i(\omega_{k'}-\omega_k)} && (1.29)\\
&= \int dk\, |\, \psi(k)|^2\, \frac{\partial \omega_k}{\partial k}\, t && (1.30)
\end{aligned}$$

$$\cong \left.\frac{\partial \omega_k}{\partial k}\right|_{k_0} t \underbrace{\int dk\, |\psi(k)|^2}_{=1}, \qquad \psi(k) \text{ centered at } k = k_0 \tag{1.31}$$

Normalized wave function:

$$\int dk\, |\psi(k)|^2 = 1 \tag{1.32}$$

$$\int dk\, |\psi(k)|^2 = \int dk \int \frac{dx'}{\sqrt{2\pi}} \frac{dx}{\sqrt{2\pi}}\, \psi^*(x')\, \psi(x) e^{-ik(x'-x)} \tag{1.33}$$

$$= \int dx' \int dx\, \delta(x - x')\, \psi^*(x')\, \psi(x) \tag{1.34}$$

$$= \int dx\, |\psi(x)|^2 = 1 \tag{1.35}$$

$$\text{and} \quad v = \frac{\partial \bar{x}}{\partial t} = \left.\frac{\partial \omega_k}{\partial k}\right|_{k_0} \tag{1.36}$$

1.2.2 Interference experiment (double slit experiment)

Historically: Interference phenomena of e^- and n-beams were observed first scattering them at crystalline structures. But the direct double slit experiment was possible only at a later time. However, crystals show the same interference effects as grids do. Therefore, we take a closer look at the double slit set up:

(a) **Figure 1.7 shows the experiment with classical particles**

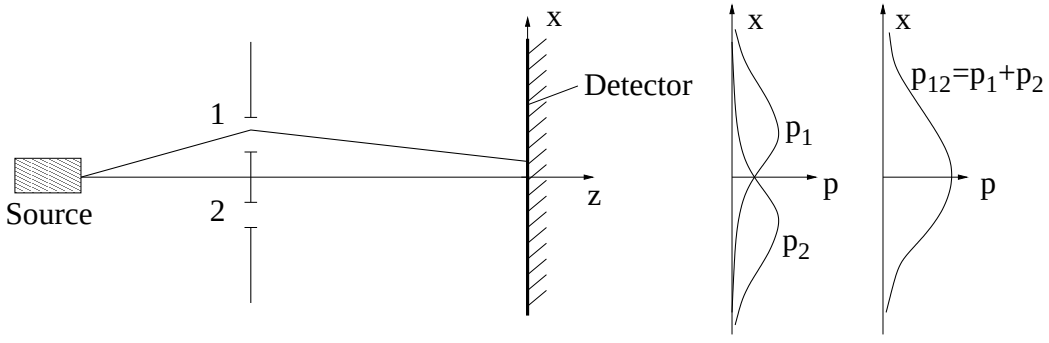

Figure 1.7: Double slit experiment with particles

No evidence of interference. The pattern of intensity on the screen is the sum of intensities $P_i,\ i = 1, 2$ of each of these 2 beams.

(b) **Figure 1.8 shows the experiment with classical waves (water, light, ...)**

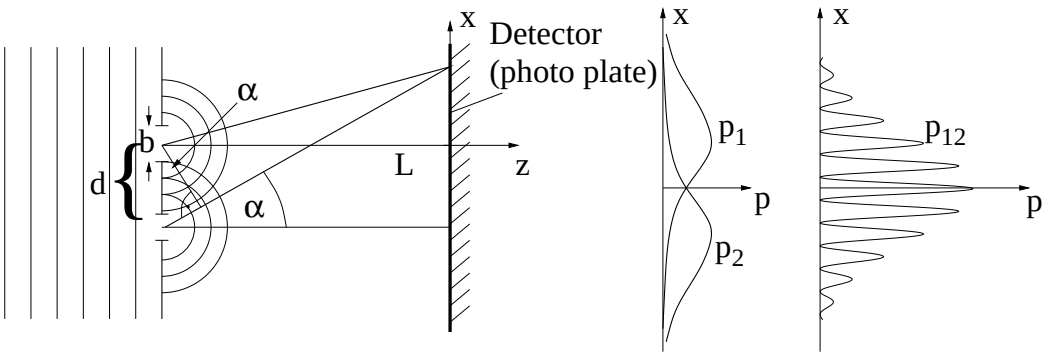

Figure 1.8: Double slit experiment with waves

Calculation of interference pattern (distribution of intensity on the screen)

Wave coming from first or second slit at position x on the screen:

$$\psi_{1,2}(x,t) = \psi_0\, e^{i(kd_{1,2}(x)-\omega t)}, \quad k = \frac{2\pi}{\lambda} \quad \text{wave number} \tag{1.37}$$

Possible paths:

$$\begin{aligned} d_1(x) &= \sqrt{L^2 + x^2} \approx L, \quad L \gg x && (1.38)\\ d_2(x) &= d_1 + d\,\sin(\alpha) && (1.39)\\ &\approx d_1 + \frac{d}{L}\,x, \quad x = L\,\tan(\alpha) \approx L\,\sin(\alpha), \quad \alpha \ll 1 && (1.40) \end{aligned}$$

Total intensity at position x on the screen (Linear superposition of amplitudes):

$$\begin{aligned} I(x) &= |\,\psi_1(x,t) + \psi_2(x,t)|^2 && (1.41)\\ &= |\psi_0|^2 \cdot |\,e^{i(kd_1-\omega t)}|^2 \cdot |1 + e^{ik\frac{d}{L}x}|^2 && (1.42)\\ &= 2\,|\psi_0|^2\,[1 + \cos(\tfrac{2\pi}{\lambda}\tfrac{d}{L}x)] && (1.43) \end{aligned}$$

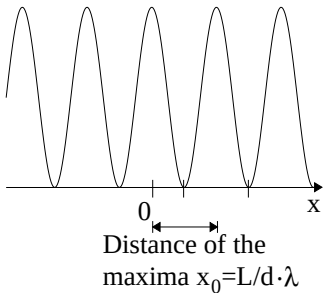

Figure 1.9: Expected amplitude of intensity pattern

(In contrast to figure 1.9 we have a subsiding modulated amplitude with increasing x. In the experiment: Result of finite coherence length)

(c) **Double slit experiment with microscopic particles of matter (electrons)**

The pattern of interference is equivalent to waves of light.

$$\boxed{\Rightarrow \text{Matter shows wave properties}} \tag{1.44}$$

Energy $E = \frac{p^2}{2m}$, momentum p and wavelength λ directly measurable in the double slit experiment (from distance of maxima):

$$\boxed{p = \hbar \frac{2\pi}{\lambda} = \hbar k} \quad \text{(de Broglie-wavelength)} \tag{1.45}$$

Energy-frequency-relation needs correlation of wave number k and frequency ω of e^- . Integration of group velocity and the particle velocity $v = \frac{\partial \omega_k}{\partial k}$ results in the desired equation:

$$\frac{p}{m} = \hbar \frac{\partial \omega_p}{\partial p}; \quad p = \hbar k, \quad v = \frac{p}{m} \tag{1.46}$$

$$\Rightarrow \quad \hbar\omega = \frac{p^2}{2m} + E_0 = E_{\text{kin}} + mc^2 \tag{1.47}$$

$$\Rightarrow \quad \boxed{\hbar\omega = E} \tag{1.48}$$

The constant of integration is defined as the energy of electrons at rest, $E_0 = mc^2$

Annotations: The reference point of energy (E - origin) as well as the frequency ω of particles can be chosen at will. This arbitrariness is expressed in the integration constant E_0 . Therefore, within non-relativistic calculations, the resting energy can be omitted.

If the intensity of the incoming beam at the double slit experiment (light or matter) is chosen sufficiently small, the continuous intensity distribution on the screen turns into a discrete accumulation of points (on the detector); see figure 1.10.

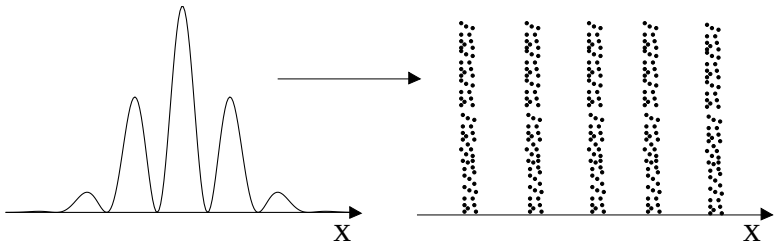

Figure 1.10: Intensity distribution of the double slit experiment

That is, light and electrons on the detector are realized as particles (a chemical reaction of a single molecule, similar to the photo effect)

⇒ Intensity $|\psi|^2$ of interference pattern returns the probability of a photon or electron to be measured at position x on the screen.

1.2.3 Further experiments

(a) **Compton effect** (see figure 1.11)
Non-elastic scattering of light at (resting) electrons.

The wavelength of light encounters a change through the scattering process which can be understood as a reduction of the photo-momentum because of

the recoil. A direct relation between the photo-momentum and wavelength can be derived from this.

(b) **Cavity radiation** (see figure 1.11)
Radiation in thermodynamical equilibrium with its environment (temperature T).

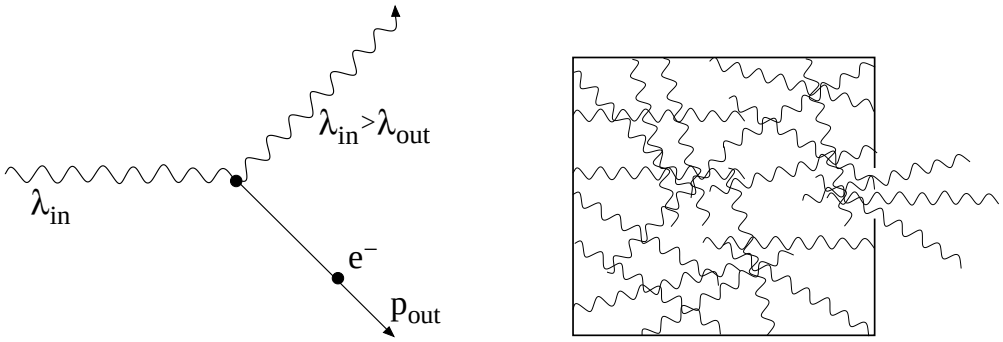

Figure 1.11: Compton scattering / Radiation in thermodynamical equilibrium

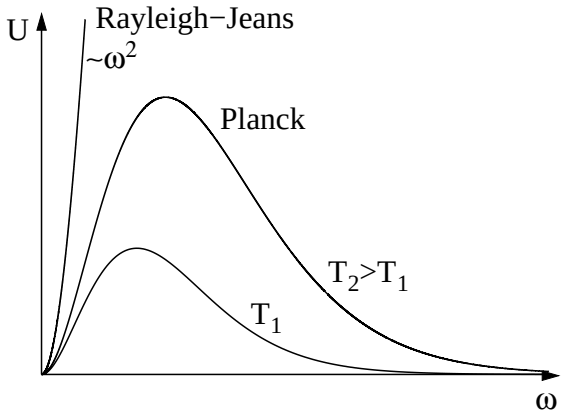

Figure 1.12: Spectral energy desnity

Raleigh-Jeans:

$$U(\omega) = \frac{k_B T}{\pi^2 c^3}\,\omega^2 \tag{1.49}$$

$$E_{\text{tot}} = \int d\omega\, U \to \infty \qquad \text{UV-disaster} \tag{1.50}$$

Planck (1900):

Postulated quantized energy of radiation for given energy $E = n\hbar\omega$ (avoids particle - interpretation).

Substitute:

$$k_B T \to \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \to \text{Fit } \hbar \tag{1.51}$$

(c) **Modern experiments**:

- Interference of atomic beams
- Direct measurement of the wave function with STM

1.2.4 Conclusions

(1) Light and matter show particle as well as wave properties (wave-particle dualism). Depending on the experiment, one or the other property can be observed.

For example:

Experiment	light	matter
Photo-effect	particle	particle
Double slit	wave	wave

Table 1.1: The wave-particle dualism

In general, the following applies to light and matter:

$$p = \hbar k = \frac{2\pi}{\lambda}\hbar \qquad \lambda = \text{de Broglie wavelength} \tag{1.52}$$

$$E = \hbar\omega, \tag{1.53}$$

where

$$E = pc \qquad \text{(light)} \tag{1.54}$$

$$= \frac{p^2}{2m} + E_0 \quad \text{(matter)}. \tag{1.55}$$

(Energy-momentum relation → frequency-wavelength relation, dispersion)

The theoretical consequences will be discussed in detail:

- Quantum physical reality depends on the experiment (observer).
- Causality and determinism (why does e^- propagating through slit 1 "know" whether slit 2 is open or closed?).
- Quantum mechanical objects are neither particles nor waves, but higher objects to show under certain circumstances either the one or the other property. The paradox (dualism) is not the object itself, but arises from the fact, that we (as observer) conclude with our measurements a particle or wave state (collaps of wave function). Since our brains can only grasp and interpret the classical terms, the paradox develops in us.
- Observer becomes part of observed world.

(2) Statistical interpretation:
Once the particle property is proved in an experiment, the intensity $|\psi(x)|^2$ of the respective wave function $\psi(x,t)$ reveals the probability density to measure the particle at x. $\psi(x,t)$ is therefore called the wave function of the particle.

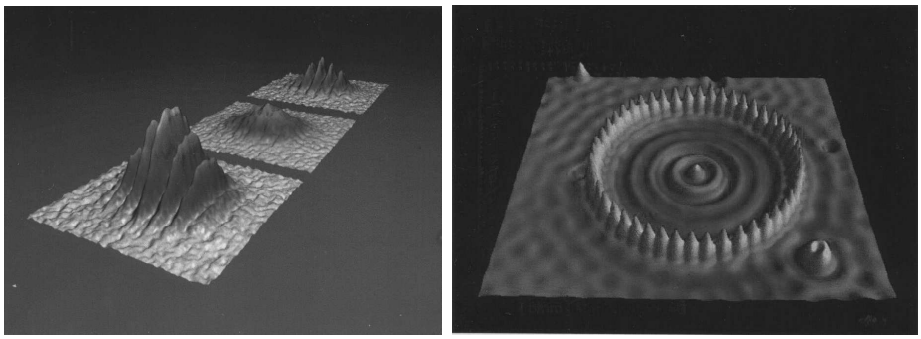

Figure 1.13: Left side: Electron wave packets on a metal surface. Right side: Electron wave in a ferroatomic ring on top of a copper layer.

(3) The intensity (= probability density) has to be normalized:

$$\int dx\, |\psi(x,t)|^2 = 1, \quad \forall t \tag{1.56}$$

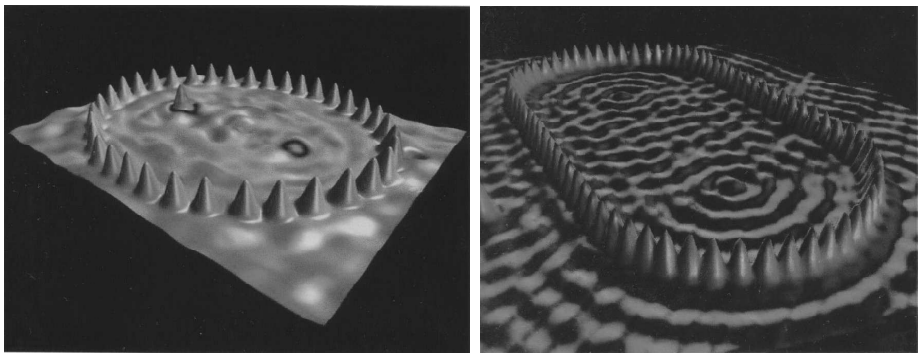

Figure 1.14: Probability density with electron waves

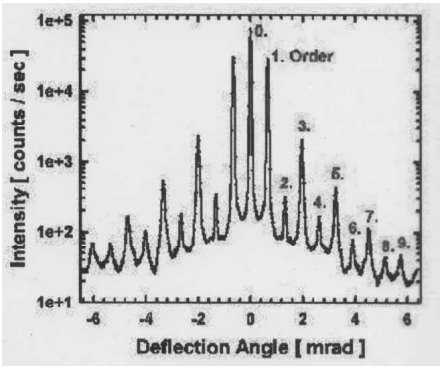

Figure 1.15: Helium atomic beam diffraction by a 100 nm-period transmission grating

Calculation of the mean for many measurements:

$$\bar{x} = \int dx\, x\, |\psi(x)|^2 \tag{1.57}$$

(4) Principle of superposition:
If $\psi_1(x,t)$, $\psi_2(x,t)$ are two wave functions (and let marginal terms for slit 1/2 open/closed be given), then also $\psi_1(x,t) + \psi_2(x,t) = \psi(x,t)$ is a possible wave function. The equation of motion for the wave function has to be linear.

1.2.5 Schrödinger equation, energy, momentum operator

We approach now the question, how the energy, the momentum and the equation of motion can be determined mathematically, if the wave function is given (heuristic approach).

Plane wave (has defined p, E):
We look for the differential equation

$$\psi(\vec{x},t) = \psi_0\, e^{i(\vec{k}\vec{x}-\omega t)}. \tag{1.58}$$

Which "operator" has to be applied on ψ such that the energy $\hbar\omega$ and the momentum are received as pre-factors?

$$i\hbar\,\frac{\partial}{\partial t}\,\psi(\vec{x},t) = i\hbar\,\frac{\partial}{\partial t}\,\psi_0\, e^{i(\vec{k}\vec{x}-\omega t)} = \hbar\,\omega\,\psi(\vec{x},t) \tag{1.59}$$

$$-i\hbar\,\nabla\psi(\vec{x},t) = -i\hbar\,\nabla\psi_0\, e^{i(\vec{k}\vec{x}-\omega t)} = \hbar\vec{k}\,\psi(\vec{x},t) \tag{1.60}$$

Energy-operator:

$$\widehat{E} = i\hbar\,\frac{\partial}{\partial t} \tag{1.61}$$

Momentum-operator:

$$\widehat{\vec{p}} = -i\hbar\,\nabla \tag{1.62}$$

For free matter particles, we have:

$$E = \frac{\vec{p}^{\,2}}{2m} \tag{1.63}$$

As a result, the plane matter-wave of a free particle with mass m has to follow the equation of motion:

$$i\hbar\,\frac{\partial}{\partial t}\,\psi(\vec{x},t) = \frac{(-i\hbar\nabla)^2}{2m}\,\psi(\vec{x},t) \tag{1.64}$$

$$\widehat{E}\psi = \frac{\widehat{\vec{p}}^{\,2}}{2m}\,\psi \tag{1.65}$$

In case the particle is moving within a potential $V(\vec{x})$, we postulate that the total energy is the sum of the kinetic and the potential energy (Schrödinger) and

we get:

$$\boxed{\begin{aligned} \widehat{E}\psi &= \left[\frac{\widehat{\vec{p}}^{\,2}}{2m} + V(\vec{x})\right]\psi \\ i\hbar\,\frac{\partial}{\partial t}\,\psi(\vec{x},t) &= \left[-\frac{\hbar^2}{2m}\,\nabla^2 + V(\vec{x})\right]\psi(\vec{x},t) \end{aligned}} \tag{1.66}$$

Remarks:

(1) Schrödinger equation has to be homogenous, because of probability conservation. This equation is the most simplest including also the special case of free particles.

(2) Schrödinger equation has to be linear → Principle of superposition.

Chapter 2

The Postulates of Quantum Theory

2.1 Mathematical basics

Chapter one introduced the wave function $\psi(x,t)$, which forms a vector space according to the principle of superposition (to add another wave function or multiply with numbers). Furthermore, it proved to be useful to define a mapping through so called "operators", who act on the vector space. Now, we will discuss several mathematical structures and define the postulates of quantum mathematics afterwards.

2.1.1 Vector space (of finite dimension)

Definition: The vector space $\mathbb{V}$ is the number of vectors $\mathbb{V} = \{|v\rangle\}$, which obey the vector-addition and scalar multiplication, such that:

$$|\,v\rangle + |\,w\rangle \;=\; |\,u\rangle, \quad \forall\, |\,v\rangle, |\,w\rangle \in \mathbb{V} \tag{2.1}$$

$$a\,|\,v\rangle \;=\; |\,w\rangle, \quad \forall\, a \in \mathbb{R} \quad \text{or} \quad \mathbb{C} \tag{2.2}$$

For the axioms follows:

1. Completeness:

$$|\,v\rangle + |\,w\rangle \in \mathbb{V} \qquad \text{and} \qquad a\,|\,v\rangle \in \mathbb{V} \tag{2.3}$$

2. Commutation relation:

$$|\,v\rangle + |\,w\rangle = |\,w\rangle + |\,v\rangle \tag{2.4}$$

3. Compatibility of addition:

$$|\,v\rangle + (|\,w\rangle + |\,u\rangle) = (|\,v\rangle + |\,w\rangle) + |\,u\rangle \tag{2.5}$$

4. Distributivity of scalar-multiplication:

$$\begin{aligned} (a+b)|\,v\rangle &= a|\,v\rangle + b|\,v\rangle & (2.6)\\ a\,(|\,v\rangle + |\,w\rangle) &= a|\,v\rangle + a|\,w\rangle & (2.7) \end{aligned}$$

5. Compatibility of multiplication:

$$a\,(b|\,v\rangle) = (ab)\,|\,v\rangle \tag{2.8}$$

6. Zero-vector:

$$\exists!\,|\,0\rangle : |\,v\rangle + |\,0\rangle = |\,v\rangle \tag{2.9}$$

7. Inverse element of addition:

$$\forall\,|\,v\rangle \in \mathbb{V}\ \exists\,|-v\rangle\,\epsilon\,\mathbb{V}: \quad |\,v\rangle + |-v\rangle = |\,0\rangle \tag{2.10}$$

$\mathbb{V}$ is real (complex), if the scalar $a \in \mathbb{R}$ ($a \in \mathbb{C}$).

Expansion in basis, coordinate representation

A Basis $\mathbb{B} = \{|\,k\rangle|\ k = 1, ..., N\}$ is the number of vectors $|\,k\rangle \in \mathbb{V}$ with the properties:

1. Every vector $|\,v\rangle \in \mathbb{V}$ represents a linear combination of $|\,k\rangle$:

$$|\,v\rangle = \sum_{k=1}^{N} v_k|\,k\rangle, \qquad \forall\,|\,v\rangle \in \mathbb{V},\, v_k \in \mathbb{R}, \mathbb{C} \tag{2.11}$$

2. Uniqueness:

$$\nexists \{a_{k'} \in \mathbb{R}, \mathbb{C} | \, k' \neq k\} \quad \text{such that} \quad |\, k\rangle = \sum_{\substack{k'=1,..,N \\ k' \neq k}} a_{k'} \, |\, k'\rangle \tag{2.12}$$

$\Rightarrow$ We have a unique basis-expansion. The number of basis vectors N is characteristic of $\mathbb{V}$ and is called dimension (proof by inconsistency).

Coordinate-representation:

Let a basis $\mathbb{B}$ be given. Hence, to every vector $|\, v\rangle \in \mathbb{V}$ we can assign (considering equation (2.11)) an array of N numbers (coordinates):

$$|\, v\rangle \overset{\text{bijective}}{\longleftrightarrow} \vec{v} = (v_1, ..., v_N)^T \tag{2.13}$$

Regulations for vector-addition and multiplication are valid for array components $\vec{v} = (v_1, ..., v_N)^T$ as well.

$\Rightarrow$ Vector space of N-arrays is isomorphic to the vector space $\mathbb{V} = \{|\, v\rangle\}$.
$\Rightarrow$ All properties of $\mathbb{V}$ can be demonstrated with N-arrays as shown in figure 2.1 and then transferred onto the abstract space $\mathbb{V}$.

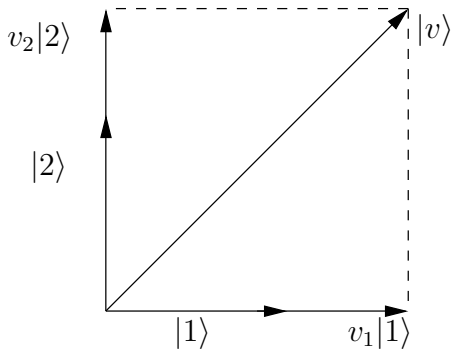

Figure 2.1: Correlation of $\mathbb{V}$ and N-array

2.1.2 Linear operators on $\mathbb{V}$

First of all we consider a mapping A: $\mathbb{V} \to \mathbb{V}$ such that $A|\,v\rangle = |\,w\rangle$. Further more we claim that A is linear, i.e.:

$$A\left(|\,v\rangle + |\,w\rangle\right) = A|\,v\rangle + A|\,w\rangle \tag{2.14}$$

$$A\left(a|\,v\rangle\right) = a\left(A|\,v\rangle\right) \tag{2.15}$$

In coordinate representation with chosen basis, the linear map is given by:

$$A|\,k\rangle = |\,u\rangle_k = \sum_{l=1}^{N} |\,l\rangle\, a_{lk}, \tag{2.16}$$

with the matrix entries

$$A = (a_{kl}) = \begin{pmatrix} a_{11} & \dots & a_{1N} \\ \vdots & & \vdots \\ a_{N1} & \dots & a_{NN} \end{pmatrix}. \tag{2.17}$$

Because of linearity, we can apply the common rules of matrix-multiplication and -addition.

2.1.3 Scalar-product and dual space

Definition: Scalar-product (Inner product)

Let a bilinear map

$$(\mathbb{V}, \mathbb{V}) \to \mathbb{R}, \mathbb{C} \tag{2.18}$$

$$(|\,v\rangle, |\,w\rangle) \to a \in \mathbb{R}, \mathbb{C} \tag{2.19}$$

be given for which the following notation will be used:

$$\langle v\,|\,w\rangle \to a \in \mathbb{R}, \mathbb{C} \tag{2.20}$$

This map has the following properties:

$$\langle v\,|\,w\rangle = \langle w\,|\,v\rangle^* \tag{2.21}$$

$$\langle v\,|\,v\rangle \geq 0 \qquad \text{(positive semi-definite)} \tag{2.22}$$

$$\langle v\,|\,(a|\,w\rangle + b|\,u\rangle) = a\,\langle v\,|\,w\rangle + b\,\langle v\,|\,u\rangle \tag{2.23}$$

(Property 1 is a consequence of the linearity in the first argument (bilinear))

Definition: Norm

$$|v| = \sqrt{\langle v \,|\, v\rangle} \qquad \text{is length of} \qquad |\, v\rangle \tag{2.24}$$

Expansion in orthonormal-basis $\mathbb{B} = \{|\, k\rangle\}$:

Choose a basis such that

$$\langle k \,|\, k'\rangle = \delta_{kk'} \tag{2.25}$$

and

$$|\, v\rangle = \sum_{k=1}^{N} v_k |\, k\rangle, \tag{2.26}$$

where the coefficients are given by

$$\langle k \,|\, v\rangle = \sum_{k'=1}^{N} v_{k'} \langle k \,|\, k'\rangle = v_k. \tag{2.27}$$

Matrix elements of an operator A with orthonormal-basis $\mathbb{B} = \{|\, k\rangle\}$:

$$A|\, k\rangle = \sum_{l=1}^{N} a_{lk} |\, l\rangle \tag{2.28}$$

$$\langle k'|A|\, k\rangle = \sum_{l=1}^{N} a_{lk} \langle k'|\, l\rangle = a_{k'k} \tag{2.29}$$

Hermitian conjugate operator

If A is defined by (a_{kl}), the hermitian conjugate operator for A is defined by

$$A^+ = (A^\intercal)^* = (a_{kl}^*) \qquad \text{and} \qquad (A^+)^+ = A. \tag{2.30}$$

For an arbitrary orthonormal-basis the scalar-product of two vectors reads:

$$|\, v\rangle = \sum_{k=1}^{N} v_k |\, k\rangle, \quad |\, w\rangle = \sum_{k'=1}^{N} w_{k'} |\, k'\rangle \tag{2.31}$$

$$\Rightarrow \langle v \,|\, w\rangle = \sum_{k,k'=1}^{N} v_k^* w_{k'} \langle k \,|\, k'\rangle = \sum_{k=1}^{N} v_k^* w_k \tag{2.32}$$

This is the well-known cartesian scalar-product:

$$\langle v \,|\, w\rangle = (v_1^*, ..., v_N^*) \begin{pmatrix} w_1 \\ \vdots \\ w_N \end{pmatrix} = \sum_{k=1}^{N} v_k^* w_k \tag{2.33}$$

The line-vectors $(v_1^*, ..., v_N^*) = \begin{pmatrix} v_1 \\ \vdots \\ v_N \end{pmatrix}^\dagger$ are hermitian conjugate vectors to the column vectors (hermitian conjugate = transpose + complex conjugate). Therefore, $\langle v \,| = |\, v\rangle^+$ can be identified with the hermitian conjugate vector to $|\, v\rangle$.

Definition: The space of hermitian conjugate vectors $\{\langle v|\} = \overline{\mathbb{V}}$ (line-vectors) is the dual space to the vector-space $\mathbb{V} = \{|\, v\rangle\}$.

Why is useful to make this distinction?

Here we want to find out what the effect of the linear operator $\langle v \,|\, (A|\, w\rangle)$. Let $|\, v\rangle$, $|\, w\rangle$ be arbitrary vectors:

$$|\, w\rangle = \sum_{k=1}^{N} w_k |\, k\rangle \tag{2.34}$$

$$A|\, w\rangle = \sum_{k=1}^{N} w_k\, A|\, k\rangle = \sum_{l,k=1}^{N} |\, l\rangle\, a_{lk} w_k \tag{2.35}$$

Or in detail:

$$A|\, w\rangle = \begin{pmatrix} a_{11} & \cdots & a_{1N} \\ \vdots & & \vdots \\ a_{N1} & \cdots & a_{NN} \end{pmatrix} \begin{pmatrix} w_1 \\ \vdots \\ w_N \end{pmatrix} = \begin{pmatrix} \sum_{k=1}^{N} a_{1k} w_k \\ \vdots \\ \sum_{k=1}^{N} a_{Nk} w_k \end{pmatrix} \tag{2.36}$$

It follows:

$$\langle v \,|\, (A|\, w\rangle) = \sum_{m,k,l} v_m^* a_{lk} w_k \langle m \,|\, l\rangle = \sum_{k,l} v_l^* a_{lk} w_k \tag{2.37}$$

$$= (\langle v \,|A) \,|\, w\rangle = \sum_{k,l} \left(\left(a_{kl}^T\right)^* v_l\right)^* w_k \tag{2.38}$$

$$= \langle A^+ v \,|\, w\rangle =: \langle v \,|A|\, w\rangle \tag{2.39}$$

$\Rightarrow$ If A operates in the direct space, A^+ has an effect in the dual space.

In detail:

$$(v_1^*, \ldots, v_N^*) \begin{pmatrix} a_{11} & \cdots & a_{1N} \\ \vdots & & \vdots \\ a_{N1} & \cdots & a_{NN} \end{pmatrix} \begin{pmatrix} w_1 \\ \vdots \\ w_N \end{pmatrix} \tag{2.40}$$

Dirac-notation:

$$\underbrace{\langle\ v\ |\ A\ |\ w\ \rangle}_{\text{bra - c - ket}} \tag{2.41}$$

2.1.4 Schwarz- and triangle-inequality

1. **Schwarz-inequality**

$$\boxed{|\langle v\,|\,w\rangle| \leq |v| \cdot |w|} \tag{2.42}$$

The value of the scalar-product of two vectors can not be greater than the product of their lengths, as it is shown in figure 2.2.

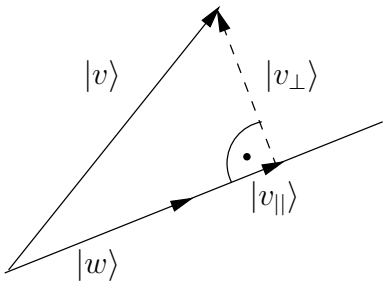

Figure 2.2: Vector representation of the Schwarz-inequality

$$|\langle v|w\rangle| = |v_{||}| \cdot |w| \tag{2.43}$$
$$\leq |v| \cdot |w| \tag{2.44}$$

The equality holds if and only if

$$|v\rangle = \lambda \cdot |w\rangle. \tag{2.45}$$

Usage of bra-c-ket-notation: bra: $\langle v\,|$ ket: $|\,v\rangle$

Let $|\,n\rangle$ be an arbitrary normalized vector, i.e. $\langle n\,|\,n\rangle = 1$. $|\,n\rangle$ is an element of the orthonormal basis $\mathbb{B} = \{|\,n\rangle\}$ (if not, choose $|\,n\rangle = \frac{|\,\widetilde{n}\rangle}{\sqrt{\langle n\,|\,n\rangle}}$, which is a normalized vector).

Then, $\widehat{P_n} = |\,n\rangle\langle n\,|$ is the projector on $|\,n\rangle$ with the projection property

$$\widehat{P}_n^2 = |\,n\rangle\langle n\,|\,n\rangle\langle n\,| = |\,n\rangle\langle n\,|, \tag{2.46}$$

such that $|\,n\rangle\langle n\,|$ projects each vector $|\,v\rangle$ on its component along $|\,n\rangle$, i.e.:

$$|\,n\rangle \underbrace{\langle n\,|\,v\rangle}_{v_n} = \underbrace{v_n}_{\substack{n\text{-th}\\ \text{component}}} |\,n\rangle \tag{2.47}$$

In detail: Coordinate-representation with basis $\{|\,n\rangle\}$

$$|\,n\rangle\langle n\,| \;\widehat{=}\; \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix} (0,\ldots,1,\ldots,0) \quad \text{and} \tag{2.48}$$

$$|v\rangle \;=\; \begin{pmatrix} v_1 \\ \vdots \\ v_n \\ \vdots \\ v_N \end{pmatrix} \tag{2.49}$$

$$|\,n\rangle\langle n\,|\,v\rangle \;\widehat{=}\; \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix} (0,\ldots,1,\ldots,0) \begin{pmatrix} v_1 \\ \vdots \\ v_n \\ \vdots \\ v_N \end{pmatrix} \tag{2.50}$$

$$= \; v_n \begin{pmatrix} 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \end{pmatrix} = v_n|\,n\rangle \tag{2.51}$$

Sum over all projectors on orthonormal basis vector:

$$\sum_{n=1}^{N} |\, n\rangle\langle n\,| = \mathbb{1} \quad \text{(completeness)} \tag{2.52}$$

$$\langle n\,|\, n\rangle = 1 \quad \text{(normalization)} \tag{2.53}$$

Expansion in orthonormal basis: "Insertion of basis"

$$|\, v\rangle = 1|\, v\rangle = \sum_{n=1}^{N} |\, n\rangle \underbrace{\langle n\,|\, v\rangle}_{v_n}, \tag{2.54}$$

matrix elements of an operator A in orthonormal basis.

Proof: Split $|\, v\rangle$ into components parallel and perpendicular to $|\, w\rangle$.

$$|\, v_\perp\rangle = |\, v\rangle - |\, w\rangle \frac{\langle w\,|\, v\rangle}{\langle w\,|\, w\rangle} \tag{2.55}$$

$$|\, v_\parallel\rangle = |\, w\rangle \frac{\langle w\,|\, v\rangle}{\langle w\,|\, w\rangle} \tag{2.56}$$

$$|\, v\rangle = |\, v_\perp\rangle + |\, v_\parallel\rangle, \tag{2.57}$$

where $\frac{|\, w\rangle}{\langle w\,|\, w\rangle}$ is a unit vector parallel to $|\, w\rangle$ and $\frac{|\, w\rangle\langle w\,|}{\langle w\,|\, w\rangle}$ is the projector on $|\, w\rangle$. Then one yields

$$\langle v\,|\, w\rangle = \langle v_\parallel\,|\, w\rangle + \langle v_\perp\,|\, w\rangle = \langle v_\parallel\,|\, w\rangle \tag{2.58}$$

with

$$\langle v_\perp\,|\, w\rangle = \langle v\,|\, w\rangle - \langle w\,|\, w\rangle \frac{\langle w\,|\, v\rangle}{\langle w\,|\, w\rangle} = 0. \tag{2.59}$$

One the other hand one finds

$$0 \le \langle v_\perp\,|\, v_\perp\rangle = \langle v - \frac{\langle w\,|\, v\rangle}{\langle w\,|\, w\rangle}\, w| \cdot |\, v - \frac{\langle w\,|\, v\rangle}{\langle w\,|\, w\rangle}\, w\rangle \tag{2.60}$$

$$= \langle v\,|\, v\rangle - \frac{\langle w\,|\, v\rangle^* \langle w\,|\, v\rangle}{\langle w\,|\, w\rangle} - \frac{\langle w\,|\, v\rangle \langle w\,|\, v\rangle^*}{\langle w\,|\, w\rangle} + \frac{\langle w\,|\, v\rangle^* \langle w\,|\, v\rangle \langle w\,|\, w\rangle}{\langle w\,|\, w\rangle^2} \tag{2.61}$$

$$= \langle v\,|\, v\rangle - \frac{\langle w\,|\, v\rangle \langle v\,|\, w\rangle}{\langle w\,|\, w\rangle} \tag{2.62}$$

and therefore gets

$$\langle v \,|\, v\rangle \;\geq\; \frac{\langle w \,|\, v\rangle\langle v \,|\, w\rangle}{\langle w \,|\, w\rangle} \tag{2.63}$$

$$\sqrt{\langle v \,|\, v\rangle}\sqrt{\langle w \,|\, w\rangle} \;\geq\; |\langle w \,|\, v\rangle|. \tag{2.64}$$

2. **Triangle-inequality**

$$\boxed{||\, v\rangle + |\, w\rangle| \leq |v| + |w|} \tag{2.65}$$

The equality is given, if $|\, v\rangle = \lambda|\, w\rangle$, i.e. if the vectors are parallel.

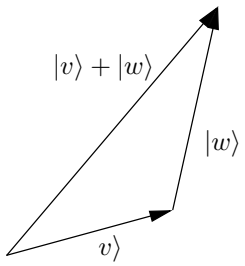

Figure 2.3: Vector representation of the triangle-inequality

2.1.5 Hermitian, anti-hermitian and unitary operators

H hermitian:

$$H^\dagger = H \tag{2.66}$$

A anti-hermitian:

$$A^\dagger = -A \qquad (\text{if} \quad A \quad \text{real} \Rightarrow \dagger = T) \tag{2.67}$$

Every operator Ω can be split up into a hermitian and anti-hermitian part:

$$H \;=\; \tfrac{1}{2}(\Omega + \Omega^\dagger) \quad \text{hermitian} \tag{2.68}$$

$$A \;=\; \tfrac{1}{2}(\Omega - \Omega^\dagger) \quad \text{anti-hermitian} \tag{2.69}$$

$$\text{with} \qquad \Omega \;=\; H + A \tag{2.70}$$

U unitary:

$$|U|v\rangle| = |v|, \qquad \forall|v\rangle \quad \text{norm invariant} \tag{2.71}$$

U is unitary if and only if

$$U^\dagger U = 1 \quad , \tag{2.72}$$

i.e. that $U^\dagger U$ is the unit operator (identity).

Proof:

$$\begin{aligned} |U|\,v\rangle|^2 &= |v|^2 = \langle v\,|\,v\rangle && (2.73)\\ \Leftrightarrow \langle Uv\,|\,Uv\rangle &= \langle v\,|U^\dagger U|\,v\rangle, \qquad \forall\,|\,v\rangle && (2.74)\\ &\Leftrightarrow U^\dagger U = 1 && (2.75) \end{aligned}$$

2.1.6 The eigenvalue problem

Let Ω be a linear operator in an N-dimensional space

$$\Omega|\,v\rangle = \lambda|\,v\rangle, \tag{2.76}$$

where $|\,v\rangle$ is the eigenvector and λ the eigenvalue belonging to $|\,v\rangle$. Equation (2.76) always has N solutions for λ and $|\,v\rangle$, where two or more values of λ may be degenerated.

Proof:

$$(\Omega - \lambda\mathbb{1})\,|v\rangle = 0 \tag{2.77}$$

has solutions, if $(\Omega - \lambda\mathbb{1})$ is singulary, i.e.

$$D = \det(\Omega - \lambda\mathbb{1}). \tag{2.78}$$

D is a polynomial of order N and consequently has N complex solutions.

The hermitian operators $H = H^\dagger$ are of exceptional importance:

1. All eigenvalues λ are real.

   Proof:

$$
\begin{aligned}
H|\,v\rangle &= \lambda|\,v\rangle && (2.79)\\
\langle v\,|H|\,v\rangle &= \lambda\langle v\,|\,v\rangle && (2.80)\\
\langle v\,|H^\dagger|\,v\rangle &= \lambda^*\langle v\,|\,v\rangle && (2.81)\\
\Leftrightarrow \lambda^* &= \lambda \quad \text{real} && (2.82)
\end{aligned}
$$

2. Eigenvectors $|\,v_1\rangle, |\,v_2\rangle$ for different eigenvalues λ_1, λ_2 are orthogonal.

   Proof:

$$
\begin{aligned}
H|\,v_1\rangle &= \lambda_1|\,v_1\rangle && (2.83)\\
H|\,v_2\rangle &= \lambda_2|\,v_2\rangle && (2.84)\\
\langle v_2\,|H|\,v_1\rangle &= \lambda_1\langle v_2\,|\,v_1\rangle && (2.85)\\
\langle H^\dagger v_2\,|\,v_1\rangle &= \lambda_2^*\langle v_2\,|\,v_1\rangle = \lambda_2\langle v_2\,|\,v_1\rangle && (2.86)\\
\lambda_1 \neq \lambda_2 &\Rightarrow \langle v_2\,|\,v_1\rangle = 0 && (2.87)
\end{aligned}
$$

   Hence, an orthonormal eigenvector basis for $H = H^\dagger$ can always be found. If there are degenerate eigenvectors, the orthonormal basis can be chosen in the subspace of the degenerate eigenvectors.

3. **Transformation to an eigenvector basis: Diagonal structure**
   We look for a transformation, such that H has diagonal structure.
   Let $\mathbb{B} = |\,v_n\rangle$ be an arbitrary orthonormal basis and let $\{|n\rangle\}$ be an orthonormal eigenvector basis. One then obtains.

$$
\begin{aligned}
H|\,n\rangle &= \lambda_n|\,n\rangle && (2.88)\\
UHU^{-1}U|\,n\rangle &= \lambda_n U|\,n\rangle && (2.89)
\end{aligned}
$$

   U transforms to this basis, such that one finds in coordinate representation:

$$
U|\,n\rangle \mathrel{\widehat{=}} (0, ..., 1, ..., 0)^T \qquad (2.90)
$$

For the original basis one gets:

$$U^{-1}U|\,n\rangle = \begin{pmatrix} n_1 \\ \vdots \\ n_N \end{pmatrix} = U^{-1}(0,...,1,...,0)^T \tag{2.91}$$

$$= \begin{pmatrix} \bar{u}_{1n} \\ \vdots \\ \bar{u}_{Nn} \end{pmatrix} \quad \text{n-th column vector of } U^{-1} \tag{2.92}$$

Because of the unitarity of U, from $U^{-1} = U^\dagger$ follows the relation

$$U = (U^{-1})^\dagger. \tag{2.93}$$

The column vectors of U^{-1} are the orthonormal eigenvectors.

2.1.7 Generalization onto infinite dimensions: The Hilbert space

The amount $\mathcal{S}$ of complex functions of a support S forms a vector space due to vector addition and scalar multiplication with a complex number:

$$|f\rangle : x \mapsto f(x), \quad \forall\, x \,\epsilon\, S \tag{2.94}$$

For example:
$S =$ finite constant interval (see figure 2.4), $S = \mathbb{R}$, $S = \mathbb{R}^n$

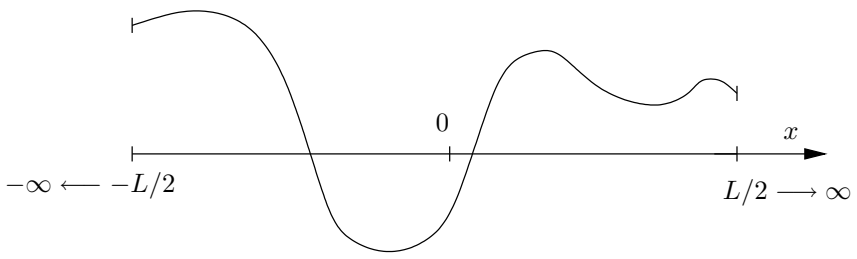

Figure 2.4: Function of support S

Scalar product: Componentwise multiplication

Integral:

$$\langle g \,|\, f \rangle = \int_{-L/2}^{+L/2} dx \; g^*(x) f(x) \tag{2.95}$$

Operators on function-space:

Position operator x: $\quad f(x) \mapsto x f(x)$
Momentum operator $pf(x) \mapsto pf(x) = -i\hbar \, \frac{\partial}{\partial x} f(x)$

Functions $f(x)$ can in every x be interpreted as vector components of f in coordinate representation, where x is the vector index of the x-th component:

$$|\, f \rangle = \begin{pmatrix} f(x_1) \\ \vdots \\ f(x_N) \end{pmatrix} \tag{2.96}$$

For continuous x:

$$x_n - x_{n-1} \;\; \rightarrow \;\; 0 \tag{2.97}$$

$$x_1 \;\; = \;\; -L/2 \tag{2.98}$$

$$x_2 \;\; = \;\; L/2 \tag{2.99}$$

Position representation: δ-function

What are the basis functions $\{|\, b_x \rangle |\, x \in S\}$ in this representation?

The arbitrary functions $f \in \mathbb{V}$ have to obey

$$f = \int dx' \; f(x') |\, b_{x'} \rangle. \tag{2.100}$$

The only function to fulfill this requirement is the "Dirac-Delta-function" (see figure 2.5)

$$\delta(x - x') = \begin{cases} 0, & x \neq x' \\ \infty, & x = x', \end{cases} \tag{2.101}$$

which has the following properties:

1. $\int dx\ \delta(x - x') = 1$
2. $\delta(x - x') = \delta(x' - x)$

Since $\infty \notin \mathbb{C}$, δ has to be defined as limit of a series of functions:

1. **Lorentz-functions**
   One definition of the δ-function is the limit

$$\delta(x - x') = \lim_{\gamma \to 0} f_\gamma(x - x'), \tag{2.102}$$

   where $f_\gamma(x - x')$ is the Lorentz-function

$$f_\gamma(x - x') = \frac{\gamma}{\pi((x - x')^2 + \gamma^2)}. \tag{2.103}$$

   $f_{\gamma \to \infty}(x)$ fulfills the properties:

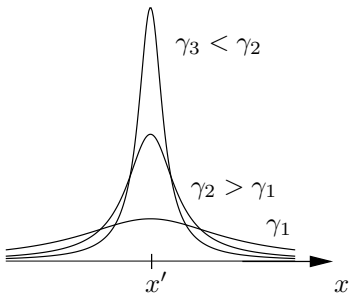

Figure 2.5: Delta-function for different γ

   - $\int dx\ f_\gamma(x) = 1 \quad \forall\ \gamma$, also $\gamma \to 0$
   - $f_\gamma(x - x') = \begin{cases} \frac{1}{\pi\gamma} & \to \infty, \quad \gamma \to 0, \quad x = x' \\ \frac{\gamma}{\pi((x-x')^2+\gamma^2)} & \to 0, \quad \gamma \to 0, \quad x \neq x' \end{cases}$

2. **Gauß-functions**

$$g_\sigma(x - x') = \lim_{\sigma \to 0} \sqrt{\frac{1}{\pi\sigma^2}}\ e^{-\frac{(x-x')^2}{\Delta^2}} \tag{2.104}$$

   Also this defintion, using the limit of the Gauß-functions, fulfills the properties of the δ-function.

The Dirac-δ-functions form per definition an orthonormal basis.

Notation:

$$|\, x_1\rangle = \delta(x - x_1), \tag{2.105}$$

where x is the variable and x_1 is an index.

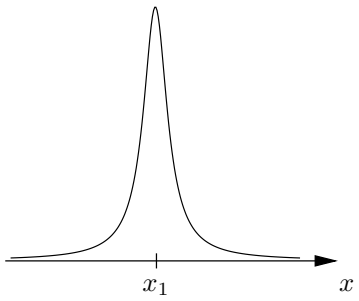

Figure 2.6: Peak at x_1 as a function of x

- Orthonormality:

$$\begin{aligned} \langle x_1 \,|\, x_2\rangle &= \int_{-\infty}^{+\infty} dx\; \delta(x - x_1)\, \delta(x - x_2) && (2.106)\\ &= \delta(x_1 - x_2) && (2.107) \end{aligned}$$

- Completeness:

$$\begin{aligned} \int dx_1 \,|\, x_1\rangle\langle x_1 \,| &= \int dx_1\; \delta(x - x_1)\, \delta(x' - x_1) && (2.108)\\ &= \delta(x - x') = 1 && (2.109) \end{aligned}$$

The Dirac-δ-functions are the eigenfunctions of the position operator $\widehat{x}$.

Matrix elements of x with respect to $\delta(x - x')$.

$$\langle x_1 \,|\widehat{x}|\, x_2\rangle = \int dx\; \delta(x - x_1)\, x\, \delta(x - x_2) = x_1\, \delta(x_1 - x_2) \tag{2.110}$$

The basis representation of the function space $\mathcal{S}$ regarding the delta functions is called **position representation**.

Momentum representation (Fourier representation)

We choose a basis $\{|\,k\rangle = \frac{1}{\sqrt{2\pi}}\, e^{ikx}|\, k \in \mathbb{R}\}$.

- Orthonormality:

$$\langle k_1\,|\,k_2\rangle = \int \frac{dx}{2\pi}\, e^{i(k_1-k_2)x} = \delta(k_1 - k_2) \tag{2.111}$$

- Completeness:

$$\int dk_1\,|\,k_1\rangle\langle k_1\,| = \int \frac{dk_1}{2\pi}\, e^{ik_1(x-x')} = \delta(x-x') = 1 \tag{2.112}$$

- An arbitrary function $|f\rangle \in \mathcal{S}$ can be represented in the basis $\{|k\rangle\}$:

$$|\,f\rangle = \int dk\; f_k\,|\,k\rangle, \tag{2.113}$$

or componentwise

$$f(x) = \int \frac{dk}{\sqrt{2\pi}}\, f_k\, e^{ikx}. \tag{2.114}$$

Convention: $f_k = f(k)$ Fourier-transformed

- The components f_k of the expansion can, because $|\,k\rangle$ is orthonormalized, be written as

$$f_k \equiv f(k) = \int \frac{dx}{\sqrt{2\pi}}\, f_x\, \underbrace{e^{-ikx}}_{|\,k\rangle^\dagger} = \langle k\,|\,f\rangle \tag{2.115}$$

the so called Fourier-transformation. The $|\,k\rangle$ are eigenfunctions of the momentum operator:

$$-i\hbar\,\vec{\nabla}\,\frac{e^{ikx}}{\sqrt{2\pi}} = \hbar k\,\frac{e^{ikx}}{\sqrt{2\pi}} \tag{2.116}$$

Hence, the Fourier-representation is called momentum-representation.

2.2 The Postulates of Quantum Theory

From the analysis of the experiments in section 1 (and many others) the following rules may be abstracted. They are *postulated* to describe the quantum world in general. Table 2.1 summarizes these rules.

(In the following the "$\widehat{\ }$" will be omitted, when it is clear that the object is an operator.)

2.3 Interpretation of Postulates: Requirements and implications

1. The *wave function* $\psi(\vec{x},t)$ of a particle in the abstract state $|\psi(t)\rangle$ is the representation of $|\psi(t)\rangle$ in the orthonormal position eigenbasis $\{|\,\vec{x}\rangle|\,\vec{x}\in\mathbb{R}^3\}$.

$$|\psi(t)\rangle = \int d^3x\,\psi(\vec{x},t)\,|\,\vec{x}\rangle \quad \text{(basis expansion)} \tag{2.117}$$

$$\psi(\vec{x},t) = \langle\vec{x}\,|\,\psi(t)\rangle \quad \text{(position representation)} \tag{2.118}$$

2. The operators $\widehat{\vec{x}},\widehat{\vec{p}}$ are *hermitian* operators, since all their eigenvalues are real.

$$\widehat{\vec{x}}\,|\,\vec{x}_1\rangle = \vec{x}_1\,|\,\vec{x}_1\rangle, \qquad \widehat{\vec{p}}\,|\,\vec{k}\rangle = \hbar\vec{k}\,|\,\vec{k}\rangle \tag{2.119}$$

with

$$\langle\vec{x}\,|\,\vec{x}_1\rangle = \delta^3(\vec{x}-\vec{x}_1) \quad \text{(position representation)}. \tag{2.120}$$

$$\langle\vec{x}\,|\,\vec{k}\rangle = \frac{1}{\sqrt{2\pi}}\,e^{i\vec{k}\vec{x}} \tag{2.121}$$

$$\widehat{\vec{p}} = -i\hbar\,\vec{\nabla} \tag{2.122}$$

$$\Rightarrow -i\hbar\,\vec{\nabla}\frac{1}{\sqrt{2\pi}}\,e^{i\vec{k}\vec{x}} = \hbar k\,\frac{e^{i\vec{k}\vec{x}}}{\sqrt{2\pi}} \tag{2.123}$$

Classical mechanics	Quantum mechanics
1. Representation of the state of a particle at time t:	
Position and momentum: $(\vec{x}(t), \vec{p}(t))$	Vector $\|\psi(t)\rangle$ in a multidimensional vector space
2. Physical observables and correspondence principle	
$\omega = \omega(\vec{x}, \vec{p})$	The independent variables $\vec{x}, \vec{p}$ are represented by hermitian operators $\vec{x} \to \widehat{\vec{x}}, \quad \vec{p} \to \widehat{\vec{p}}$. In position representation: $\langle \vec{x} \,\|\widehat{\vec{x}}\|\, \vec{x}' \rangle = \delta(\vec{x} - \vec{x}')\, \vec{x}$ $\langle \vec{x} \,\|\widehat{\vec{p}}\|\, \vec{x}' \rangle = \delta(\vec{x} - \vec{x}')\, (-i\hbar \frac{\partial}{\partial \vec{x}})$ Physical observables are functions of the operators $\vec{x}, \vec{p}$: $\widehat{\Omega} = \Omega(\widehat{\vec{x}}, \widehat{\vec{p}})$. Every observable is a hermitian operator.
3. The result of a measurement: Relation of theory to the experimental observation	
Particle in state $(\vec{x}, \vec{p})$ $\to$ Measurement of ω yields $\omega(\vec{x}, \vec{p})$ $\to$ State $(\vec{x}, \vec{p})$ remains unchanged	Particle in state $\|\psi\rangle$ $\to$ Measurement of the (hermitian) observable $\widehat{\Omega}$ yields one of the (real) eigenvalues ω of $\widehat{\Omega}$ with probability $P(\omega) = \|\langle \omega \,\|\, \psi \rangle\|^2$. $\to$ The state of the system changes to the eigenstate $\|\,\omega\rangle$ corresponding to the eigenvalue.
4. Time evolution of a state	
Hamilton equations $\frac{\partial \vec{x}}{\partial t} = \frac{\partial H}{\partial p}$ and $\frac{\partial \vec{p}}{\partial t} = -\frac{\partial H}{\partial \vec{x}}$	Schrödinger equation $i\hbar \frac{\partial}{\partial t} \|\psi(t)\rangle = \widehat{H} \,\|\psi(t)\rangle$ with $\widehat{H} = H(\vec{x} \to \widehat{\vec{x}}, \vec{p} \to \widehat{\vec{p}})$

Table 2.1: Tabulated comparison of classical and quantum mechanics

3. **Probability density**

Normalizability of the wave function (Hilbert space).

As a special case of postulate 3, a position measurement returns the eigenvalue $\vec{x}$ with probability

$$|\langle \vec{x} \,|\, \psi \rangle|^2 = |\psi(\vec{x},t)|^2 = \text{modules}^{\,2} \text{ of the wave function} \tag{2.124}$$

$$= \text{probability density of finding the particle at } \vec{x} \tag{2.125}$$

$$\Rightarrow \quad \psi(\vec{x},t) \text{ must be normalized.} \tag{2.126}$$

a) For a particle in a finite region of space:

$$\psi(\vec{x},t) \to 0 \quad \text{for} \quad |\vec{x}| \to \infty \tag{2.127}$$

and a square integrable wave function $\psi(\vec{x},t)$.

$$\int d^3x \; |\psi(\vec{x},t)|^2 = 1 \quad \text{or abstract } \langle \psi \,|\, \psi \rangle = 1 \tag{2.128}$$

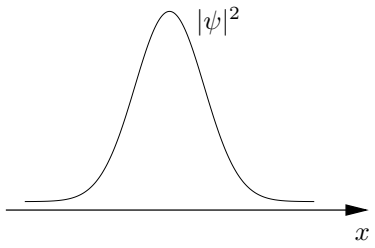

Figure 2.7: Probability density of ψ

b) For a particle distributed over infinite space (e.g. plane wave):

$$\psi_{\vec{k}}(\vec{x},t) = \frac{1}{\sqrt{2\pi}} \, e^{i(\vec{k}\vec{x} - \frac{E_k}{\hbar}t)} \quad \text{(not square integrable)} \tag{2.129}$$

We require the integrability condition

$$\int d^3x \; \psi^*(\vec{x}',t) \, \psi(\vec{x},t) = \delta(\vec{x} - \vec{x}'). \tag{2.130}$$

Interpretation: ∞ particle number in a plane wave (see figure 2.8)

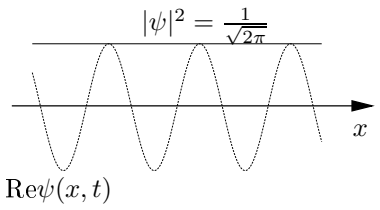

Figure 2.8: Plane wave

Definition: A vector space whose vectors are either normalized to 1 (2.128) or to $\delta(\vec{x} - \vec{x}')$ (2.130) is called **Hilbert space**.

The space of any physical states must be a Hilbert space.

4. **The measurement process, quantum reality**
   Measurement in quantum mechanics:
   The measurement apparatus is a quantum system with well defined eigenstates.

   Examples:

   - Position measurement: Photo film

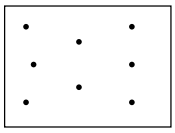

Figure 2.9: $\vec{x}$ eigenstates on a photo film

   - Velocity measurement: Wien filter

   After the measurement the particle is in a well defined $\vec{x}$ or $\vec{p}$ eigenstate. The measurement apparatus is a projector onto one of its eigenstates with probability P.

   Mathematical description of the measurement:

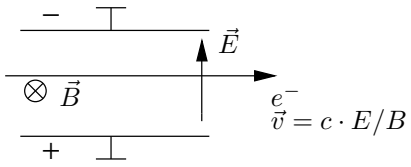

Figure 2.10: Wien filter

a) Construct quantum operator (observable) corresponding to the measurement:

$$\widehat{\Omega} = \Omega\,(\vec{x} \to \widehat{\vec{x}}, \vec{p} \to \widehat{\vec{p}}) \tag{2.131}$$

b) Find the orthonormal eigenvectors $|\,\omega_i\rangle$ with eigenvalues ω_i of $\widehat{\Omega}$.

c) Prior to the measurement, the system is in a general state $|\psi\rangle$ which can be expanded in the orthonormal eigenbasis of $\widehat{\Omega}$:

$$|\psi\rangle = \sum_i |\,\omega_i\rangle\langle\omega_i\,|\,\psi\rangle \tag{2.132}$$

This means that the system is in a superposition of eigenstates $|\,\omega_i\rangle$ with the relative amplitudes $\langle\omega_i\,|\,\psi\rangle$.

d) The measurement apparatus projects the state $|\psi\rangle$ onto one of the eigenstates $|\,\omega_m\rangle$ of $\widehat{\Omega}$:

$$\begin{aligned} P_m &= |\,\omega_m\rangle\langle\omega_m| && (2.133)\\ P_m|\psi\rangle &= \sum_i |\,\omega_m\rangle\langle\omega_m|\,\omega_i\rangle\langle\omega_i\,|\psi\rangle && (2.134)\\ &= |\,\omega_m\rangle\langle\omega_m|\psi\rangle && (2.135)\end{aligned}$$

"collapse", "reduction" of the state

After the projection the state has a reduced amplitude $\langle\omega_m|\psi\rangle$.
The probability that the particle appears after projection in eigenstate $|\,\omega_m\rangle$, i.e. that value ω_m is measured, is given by the *intensity* of the projected state,

$$P(\omega_m) = |\langle\omega_m|\psi\rangle|^2. \tag{2.136}$$

The state is changed $|\psi\rangle \to |\,\omega_m\rangle$ by the measurement, unless it has already been in an eigenstate of $\widehat{\Omega}$

Copenhagen interpretation:

- Prior to the measurement the system is in an unknown state $|\psi\rangle$.
- The outcome of a single measurement is undeterministic. Only statistical predictions about the outcome are possible.
- $|\psi\rangle$ cannot, by principle, be determined from a single measurement. Many measurements on equally prepared initial state to determine the relative weights $|\langle\omega_i\,|\,\psi\rangle|^2$ of the expansion. Even then there is in general no unique procedure to determine $\langle\omega_i\,|\,\psi\rangle$, since it has a complex phase.

Philosophical problems:

- How is the distinction between system and measurement apparatus to be made?
- Is there physical reality without the observer? Causality?
  ($\rightarrow$ Paradox: Schrödinger's cat)
- How does the projection (state collapse) work microscopically? Interaction system $\leftrightarrow$ measurement apparatus?

Expectation value:
Average value of the observable obtained in many measurements of the same quantity.

$$\langle\Omega\rangle = \sum_i P(\omega_i)\,\omega_i = \sum_i |\langle\omega_i\,|\,\psi\rangle|^2\omega_i \tag{2.137}$$

5. **Measurement of several observables**
   Different observables (operators) do in general not commute. The outcome of the measurement of 2 observables depends on the order of the projections.

   Example:
   Consider the operators $\widehat{\vec{x}}$, $\widehat{\vec{p}}$ and an ingoing plane wave $|\psi\rangle$.

   1. $\widehat{\vec{x}}\widehat{\vec{p}}|\psi\rangle$ (see figure 2.11)

$$P_xP_p|\,\psi\rangle = P_x|\,\vec{p}\rangle\langle\vec{p}\,|\,\psi\rangle = |\,x\rangle\langle x\,|\,p\rangle\langle p\,|\,\psi\rangle \tag{2.138}$$

2. $\widehat{\vec{p}}\widehat{\vec{x}}|\psi\rangle$ (see figure 2.12)

$$P_p P_x |\,\psi\rangle = P_p |\,\vec{x}\rangle\langle\vec{x}\,|\,\psi\rangle = |\,p\rangle\langle p\,|\,x\rangle\langle x\,|\,\psi\rangle \tag{2.139}$$

As it can be seen from the equations (2.139) and (2.138) these operators yield different final states.

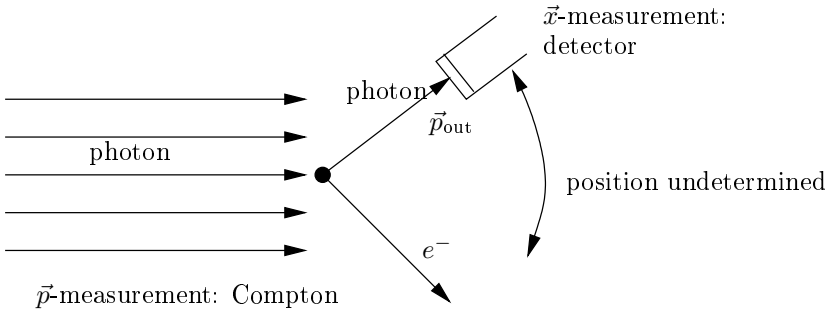

Figure 2.11: Undetermined position

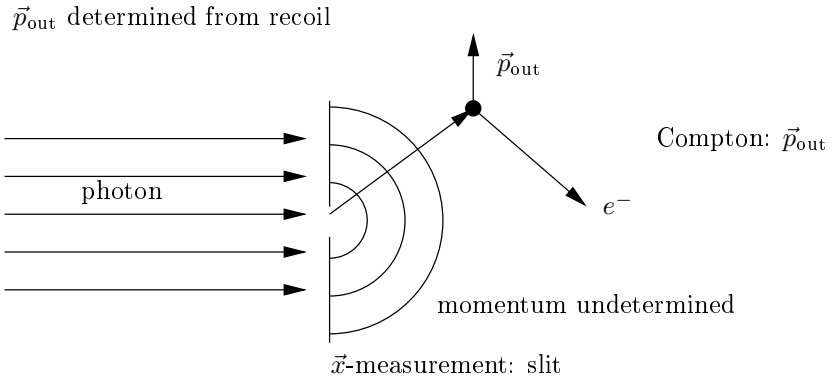

Figure 2.12: Undetermined momentum

Definition: Commutator

$$[A, B] := AB - BA \tag{2.140}$$

If $[A, B] = 0$ and A, B are hermitian operators, then there exists a common eigenbasis of A, B and the outcome of the measurement is not dependent on the order of the measurements.

Canonically conjugate operators:

$$\vec{x},\, \vec{p} = -i\hbar\, \frac{\partial}{\partial \vec{x}} \quad \text{and} \quad t,\, E = i\hbar\, \frac{\partial}{\partial t} \tag{2.141}$$

One finds for the commutator of $\vec{x}$ and $\vec{p}$:

$$\begin{aligned} [\vec{x}, \vec{p}\,]\, \psi(\vec{x}) &= -i\hbar \left(\vec{x}\, \frac{\partial}{\partial \vec{x}}\, \psi(\vec{x}) - \frac{\partial}{\partial \vec{x}}\, \vec{x}\, \psi(\vec{x}) \right) && (2.142) \\ &= -i\hbar \left(\vec{x}\, \frac{\partial}{\partial \vec{x}}\, \psi(\vec{x}) - \psi(\vec{x}) - \vec{x}\, \frac{\partial}{\partial \vec{x}}\, \psi(\vec{x}) \right) && (2.143) \\ &= \quad i\hbar \quad \psi(\vec{x}) && (2.144) \end{aligned}$$

Because $\psi(\vec{x})$ is arbitrary, the commutator reads

$$[\vec{x}, \vec{p}\,] = i\hbar\, \mathbb{1} \tag{2.145}$$

and analogous to the previous calculation one can also show that

$$[t, E] = -i\hbar\, \mathbb{1} \tag{2.146}$$

yields.

2.4 The Heisenberg uncertainty relations

Statistical treatment:	Many measurements of the same quantity $\widehat{\Omega}$ on an equally prepared initial state $\lvert\psi\rangle$.
Expectation value:	The average measured eigenvalue $\langle\Omega\rangle = \sum_i P(\omega_i)\, \omega_i = \sum_i \lvert\langle\omega_i\lvert\psi\rangle\rvert^2 \omega_i = \langle\psi\lvert\Omega\rvert\psi\rangle$
Standard deviation:	$\Delta\Omega = \sqrt{\langle\psi\rvert\, (\Omega - \langle\Omega\rangle)^2 \lvert\psi\rangle}$

If $\lvert\psi\rangle$ is not an eigenstate of $\widehat{\Omega}$, then $\Delta\Omega \neq 0$, since there is a distribution of measured eigenvalues ω_i.
If we measure another observable $\widehat{\Lambda}$ with $[\widehat{\Omega}, \widehat{\Lambda}] \neq 0$, then $\lvert\psi\rangle$, in general, won't be an eigenstate of both $\widehat{\Omega}$ and $\widehat{\Lambda}$. This may be possible in special cases.

Example: Plane wave $\langle x \,|\, \psi\rangle = \frac{1}{\sqrt{2\pi}}\, e^{ikx}$

The momentum $p = \hbar k$ is fixed and the position x completely undetermined.

Then Ω and Λ can not be *predicted simultaneously* with *arbitrary precision*. Each measurement still gives a sharp value, but varies for each measurement. This statement is made quantitatively by the Heisenberg uncertainty relations:

For a given state $|\psi\rangle$ one finds:

$$\begin{aligned}(\Delta\Omega)^2(\Delta\Lambda)^2 &= \langle\psi|\,(\Omega - \langle\Omega\rangle)^2|\psi\rangle\langle\psi|\,(\Lambda - \langle\Lambda\rangle)^2|\psi\rangle && (2.147)\\ &= \langle\psi|\,(\Delta\widehat{\Omega})^2|\psi\rangle\langle\psi|\,(\Delta\widehat{\Lambda})^2|\psi\rangle && (2.148)\\ &= \langle\Delta\widehat{\Omega}\,\psi|\underbrace{\Delta\widehat{\Omega}\,\psi}_{|v_1\rangle}\rangle\langle\Delta\widehat{\Lambda}\,\psi|\underbrace{\Delta\widehat{\Lambda}\,\psi}_{|v_2\rangle}\rangle && (2.149)\end{aligned}$$

Schwarz-inequality:

$$|\langle v_1\,|\,v_2\rangle| \leq |\,|v_1\rangle| \cdot |\,|v_2\rangle| = \sqrt{\langle v_1\,|\,v_1\rangle} \cdot \sqrt{\langle v_2\,|\,v_2\rangle} \qquad (2.150)$$

The equality holds exactly when

$$|\,v_2\rangle = c\,|\,v_1\rangle, \quad c \in \mathbb{C}. \qquad (2.151)$$

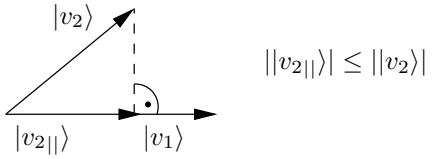

Figure 2.13: Schwarz-inequality

$$\begin{aligned}(\Delta\Omega)^2(\Delta\Lambda)^2 &\geq |\langle\Delta\widehat{\Omega}\,\psi|\Delta\widehat{\Lambda}\,\psi\rangle|^2 && (2.152)\\ &= |\langle\psi|\Delta\widehat{\Omega}\,\Delta\widehat{\Lambda}|\psi\rangle|^2 && (2.153)\end{aligned}$$

with

$$\begin{aligned}\Delta\widehat{\Omega}\,\Delta\widehat{\Lambda} &= \tfrac{1}{2}\,[(\Delta\widehat{\Omega}\,\Delta\widehat{\Lambda} + \Delta\widehat{\Lambda}\,\Delta\widehat{\Omega}) && (2.154)\\ &\quad +(\Delta\widehat{\Omega}\,\Delta\widehat{\Lambda} - \Delta\widehat{\Lambda}\,\Delta\widehat{\Omega})]\\ &= \tfrac{1}{2}\,[\Delta\widehat{\Omega},\,\Delta\widehat{\Lambda}]_+ + \tfrac{1}{2}\,[\Delta\widehat{\Omega},\,\Delta\widehat{\Lambda}] && (2.155)\end{aligned}$$

one further obtains

$$(\Delta\Omega)^2(\Delta\Lambda)^2 \geq \frac{1}{4}\underbrace{\langle\psi|\,[\Delta\widehat{\Omega},\,\Delta\widehat{\Lambda}]_+|\psi\rangle^2}_{\geq 0} + \frac{1}{4}\,\langle\psi|\,\underbrace{[\Delta\widehat{\Omega},\,\Delta\widehat{\Lambda}]}_{=i\hbar 1}\,|\psi\rangle^2. \tag{2.156}$$

LHS at least $\geq \frac{1}{4}\,\langle\psi|\,[\Delta\widehat{\Omega},\Delta\widehat{\Lambda}]\,|\psi\rangle$ for conjugated operators Ω,Λ.

$$\boxed{\Delta\Omega\cdot\Delta\Lambda \geq \tfrac{1}{2}\,\hbar} \tag{2.157}$$

Equation (2.157) is the uncertainty relation for conjugated variables.

Examples:

$$\boxed{\begin{aligned} \Delta x\cdot\Delta p &\geq \frac{1}{2}\,\hbar \quad \text{(position-momentum uncertainty)} \\ \Delta t\cdot\Delta E &\geq \frac{1}{2}\,\hbar \quad \text{(time-energy uncertainty)} \end{aligned}} \tag{2.158}$$

Remarks:

1. The equality holds exactly, if
   - $\Delta\widehat{\Omega} = c\cdot\Delta\widehat{\Lambda}|\psi\rangle$ (Schwarz inequality)
   - $\langle\psi|[\Delta\widehat{\Omega},\Delta\widehat{\Lambda}]_+|\psi\rangle = 0$
2. If $|\psi\rangle$ happens to be an eigenstate of both $\Delta\widehat{\Omega}$ and $\Delta\widehat{\Lambda}$, it follows that $\Delta\Omega\cdot\Delta\Lambda = 0$ even holds if $[\widehat{\Omega},\Lambda]\neq 0$.
3. Minimum uncertainty wave packet: $\Delta x\cdot\Delta p = \frac{1}{2}\hbar$
   $\langle x\,|\,\psi_{min}\rangle = \frac{1}{\sqrt{\pi\sigma^2}}\,e^{-\frac{x^2}{\sigma^2}}$ fulfills both requirements above.

2.5 Schrödinger equation

$$i\hbar\,\frac{\partial}{\partial t}\,|\psi(t)\rangle = H|\psi(t)\rangle \tag{2.159}$$

Properties:

a) The Schrödinger equation is a linear (partial) differential equation. Therefore the superposition principle holds.

b) If H is time independent (stationary system), then the solution is separable in time

$$|\psi(t)\rangle = |\psi\rangle \, e^{-i\frac{E}{\hbar}t} \tag{2.160}$$

and $|\psi_x\rangle$ obeys the stationary Schrödinger equation, where E is the energy of the particle,

$$\boxed{E|\psi\rangle = H|\psi\rangle}. \tag{2.161}$$

2.6 Particle density, current density and particle number conservation

Consider a state $|\psi\rangle$ in position representation $\langle \vec{x} \,|\, \psi\rangle = \psi(\vec{x}, t)$.

$$|\psi(\vec{x}, t)|^2 = \rho\,(\vec{x}, t) \;=\; \text{probability of finding a particle at } \vec{x}, t \tag{2.162}$$

$$= \text{particle density} \tag{2.163}$$

We seek to derive a continuity equation for $\rho\,(\vec{x}, t)$ and the current density $\vec{j}\,(\vec{x}, t)$ (see figure 2.14).

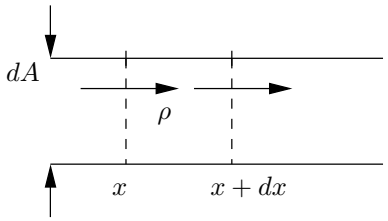

Figure 2.14: Illustration of the continuity equation

$$\frac{\partial}{\partial t}\,(\rho \cdot dx)\,dA \;=\; [j_x\,(x, t) - j_x\,(x + dx, t)]\,dA \tag{2.164}$$

$$\frac{\partial}{\partial t}\,\rho + \frac{\partial}{\partial x}\,j_x \;=\; 0 \tag{2.165}$$

In 3 dimensions one then obtains

$$\boxed{\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0}. \tag{2.166}$$

Together with

$$\begin{aligned}
\frac{\partial}{\partial t} |\psi(\vec{x},t)|^2 &= \psi^*(x,t) \left(\frac{\partial}{\partial t} \psi(\vec{x},t) \right) && (2.167)\\
&\quad + \left(\frac{\partial}{\partial t} \psi^*(\vec{x},t) \right) \psi(\vec{x},t) \\
\frac{\partial}{\partial t} \psi(\vec{x},t) &= -\frac{i}{\hbar} \left(-\frac{\hbar^2 \nabla^2}{2m} + V(\vec{x}) \right) \psi(\vec{x},t) && (2.168)\\
\frac{\partial}{\partial t} \psi^*(\vec{x},t) &= \frac{i}{\hbar} \left(-\frac{\hbar^2 \nabla^2}{2m} + V(\vec{x}) \right) \psi^*(\vec{x},t) && (2.169)
\end{aligned}$$

one further finds

$$\begin{aligned}
\frac{\partial}{\partial t} |\psi(\vec{x},t)|^2 &= -\frac{\hbar}{2mi} \left(\psi^*(x,t) \left[\nabla^2 \psi(\vec{x},t) \right] \right. && (2.170)\\
&\quad \left. - \left[\nabla^2 \psi^*(\vec{x},t) \right] \psi(\vec{x},t) \right) \\
&= -\nabla \frac{\hbar}{2mi} \left[\psi^* (\nabla \psi) - (\nabla \psi^*) \psi \right] && (2.171)
\end{aligned}$$

Particle current density:

$$\boxed{\begin{aligned}
\vec{j} &= \frac{\hbar}{2mi} \left[\psi^* (\nabla \psi) - (\nabla \psi^*) \psi \right] \\
\rho &= |\psi(x,t)|^2 \\
\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{j} &= 0
\end{aligned}} \tag{2.172}$$

Example:
For a wave with no amplitude modulation

$$\psi(x,t) = e^{i(\vec{k}\vec{x} - \omega_k t)} = e^{i(\phi(\vec{x}) - \omega_k t)} \tag{2.173}$$

one gets the current density

$$\vec{j} = \frac{\hbar}{m} \vec{\nabla} \phi(\vec{x}) \cdot \rho(\vec{x},t), \tag{2.174}$$

and for a plane wave

$$\phi(\vec{x}) = \vec{k}\vec{x} \tag{2.175}$$

furthermore

$$\vec{j} = \frac{\hbar\vec{k}}{m} \cdot \rho = \vec{v} \cdot \rho. \tag{2.176}$$

Chapter 3

Simple Problems in 1 Dimension

3.1 Particle in a Box

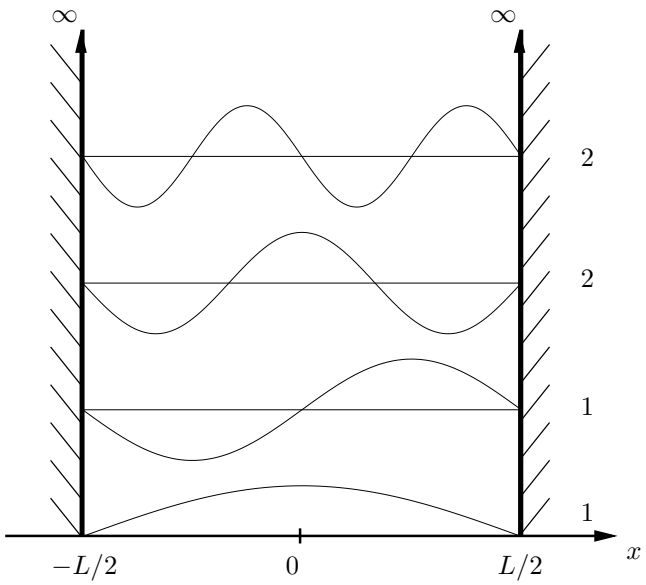

Figure 3.1: Particle in a box with infinitly high walls

The one-dimensional stationary Schrödinger equation in position representation is given by the expression

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\psi(x), \tag{3.1}$$

with a potential $V(x)$ here defined by:

$$V(x) = \begin{cases} 0, & |x| \leq L/2 \\ +\infty, & |x| > L/2 \end{cases} \tag{3.2}$$

Problems with piecewise constant potential $V(x) = V_0$ were solved by plane waves.

Ansatz:

$$\psi(x) = \psi_0 e^{ikx} \tag{3.3}$$

with

$$E = \frac{(\hbar k)^2}{2m} - V_0 \tag{3.4}$$

and

$$k = \pm\frac{1}{\hbar}\sqrt{2m(E - V_0)} \tag{3.5}$$

$$= \begin{cases} \overbrace{\pm\frac{1}{\hbar}\sqrt{2m(E - V_0)}}^{\text{oscillating solution}} & , \quad E > V_0 \\ \underbrace{\pm\frac{i}{\hbar}\sqrt{2m(V_0 - E)}}_{\text{exp. decaying solution}} = \frac{i}{\hbar}\kappa & , \quad E < V_0 \end{cases} \tag{3.6}$$

Figure 3.2: Exponentially decaying solution

For $V_0 \to \infty, \kappa \to \infty$ it follows that $\psi(x) = 0$ for $|x| > L/2$.

Matching the boundary conditions at the boundaries of the box:
Since the Schrödinger equation is second order in x,

- $\psi(x)$ is continuous and
- $\frac{\partial\psi[x]}{\partial x}$ can have a finite jump at $x = \pm L/2$, so that $\frac{\partial^2\psi}{\partial x^2} \sim \delta(x \pm L/2)$, compensating $V(x)\psi(x) \sim \delta(x \pm L/2)$.

The boundary condition therefore reads $\psi(x = \pm L/2) = 0$. Since the stationary Schrödinger equation is real, we can choose ψ real. The system includes the symmetry of parity invariance, i.e.

$$[P, H] = 0, \quad P = \pm 1. \tag{3.7}$$

The real wave function is chosen to be

$$\psi(x) = \begin{cases} \psi_0(e^{ikx} \pm e^{-ikx}), & |x| \leq L/2 \\ 0, & |x| \geq L/2 \end{cases} . \tag{3.8}$$

There exist two families of normalized solutions:

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}}\cos(k^o x), & k_n^o = \frac{(2n+1)\pi}{L} \quad n = 0, 1, 2, \ldots \\ \sqrt{\frac{2}{L}}\sin(k^e x), & k_n^e = \frac{2n\pi}{L} \quad n = 0, 1, 2, \ldots \end{cases} \tag{3.9}$$

Observations:

- Quantization of the eigenenergies E:
  The energy E_n is fixed by $E_n = \frac{(\hbar k_n^{(e/o)})^2}{2m}$. The quantization of the eigenenergies of *bound* states is induced by the boundary condition that the wave function has to vanish for $|x| \to \infty$. This is a general feature of bound states. The eigenenergies of extended states (scattering states) are not quantized, but continuous.
- Node theorem:
  The number of nodes (zeros) increases by 1 with the principal quantum number n. This is a general feature. In 2 or 3 dimensions: node lines, node surfaces.

3.2 Potential step: scattering

Consider the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi = E\psi \tag{3.10}$$

with a step potential (see figure 3.3)

$$V(x) = V_0\Theta(x). \tag{3.11}$$

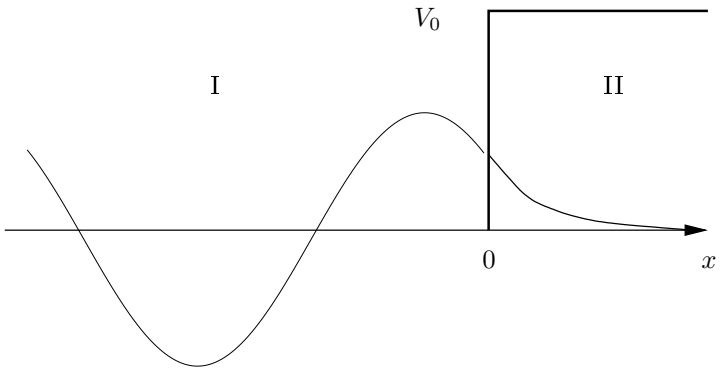

Figure 3.3: Scattering at a potential step

Since $V(x)$ is piecewise constant, one gets plane wave or exponential solutions in the regions I, II.

$$\text{Incident wave:} \quad \psi_i(x) = \psi_0 e^{i(kx-\omega t)}, \quad x < 0 \tag{3.12}$$

$$\text{Reflected wave:} \quad \psi_r(x) = r\psi_0 e^{i(-k_r x-\omega t)}, \ x < 0 \tag{3.13}$$

$$\text{Transmitted wave:} \quad \psi_t(x) = t\psi_0 e^{i(k_t x-\omega t)}, \quad x > 0, \tag{3.14}$$

where ψ_0 is set as $\psi_0 = 1/\sqrt{2\pi}$ and

$$E = \hbar\omega > 0 \quad \text{(arbitrary, fixed)} \tag{3.15}$$

$$k = \frac{1}{\hbar}\sqrt{2mE} = k_r \tag{3.16}$$

$$k_t = \begin{cases} 1/\hbar\sqrt{2m(E-V_0)} & , \quad E > V_0 \\ i/\hbar\sqrt{2m(V_0-E)} = i\kappa_t & , \quad E < V_0 \end{cases} . \tag{3.17}$$

Boundary conditions at $x = 0$:

Since it is a finite potential step, $\psi'(0)$ must exist (continuous) and $\psi''(0)$ is discontinuous. One gets

$$\psi_i(0) + \psi_r(0) = \psi_t(0) \quad \Leftrightarrow \quad 1 + r = t \tag{3.18}$$

$$\psi_i'(0) + \psi_r'(0) = \psi_t'(0) \quad \Leftrightarrow \quad ik(1 - r) = ik_t t \tag{3.19}$$

and by that

$$r = \frac{k - k_t}{k + k_t} \quad \text{(reflection amplitude)} \tag{3.20}$$

$$t = 1 + r = \frac{2k}{k + k_t} \quad \text{(transmission amplitude).} \tag{3.21}$$

In the following we will consider two special cases and will investigate the solution's structure.

1. $E > V_0$: $\quad k_t \in \mathbb{R}$

$V_0 > 0$: $\quad k_t < k, \quad r, t > 0$
No phase jump, scattering phase $\delta = 0$

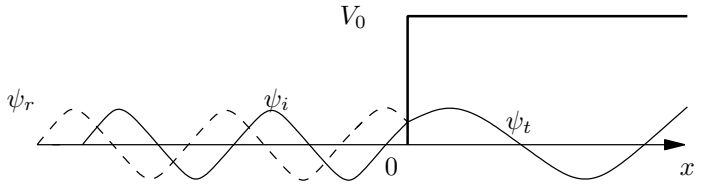

Figure 3.4: Potential step scattering with $E > V_0$ and $V_0 > 0$

$V_0 < 0$: $\quad k_t > k, \quad r < 0, t > 0$
Reflected wave has scattering phase $\delta = \pi$

Particle current:

$$j_i = \frac{\hbar}{2mi}(\psi_i^* \psi_i' - \psi_i'^* \psi_i) = \frac{\hbar k}{m}|\psi_0|^2 \tag{3.22}$$

$$j_r = -\underbrace{\frac{\hbar k}{m}}_{v_i} |r|^2 |\psi_0|^2 \tag{3.23}$$

$$j_t = \underbrace{\frac{\hbar k_t}{m}}_{v_t} |t|^2 |\psi_0|^2 \tag{3.24}$$

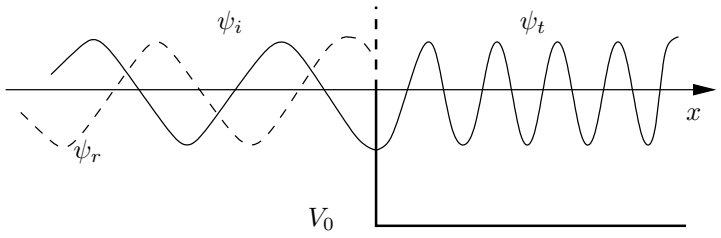

Figure 3.5: Potential step scattering with $E > V_0$ and $V_0 < 0$

Current conservation:

$$j_i + j_r = \frac{\hbar k}{m}(1 - |r|^2)|\psi_0|^2 = \frac{\hbar k}{m}\frac{4kk_t}{(k+k_t)^2}|\psi_0|^2 \tag{3.25}$$

$$j_t = \frac{\hbar k_t}{m}\frac{4k^2}{(k+k_t)^2}|\psi_0|^2 = j_i + j_r \tag{3.26}$$

2. $E < V_0$: $\quad k_t = i\kappa_t, \kappa_t \in \mathbb{R}$

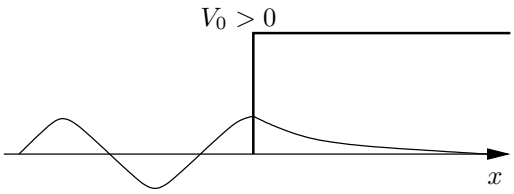

Figure 3.6: Potential step scattering with $E < V_0$

$$|r|^2 = \left|\frac{k - i\kappa_t}{k + i\kappa_t}\right|^2 = 1 \tag{3.27}$$

$$j_r = -j_i \tag{3.28}$$

$$j_t(x \to +\infty) = 0 \tag{3.29}$$

Equation (3.28) says that all particles are reflected and equation (3.29) says that the wave function decays exponentially for $x \to \infty$. The particles penetrate into the barrier, which is classical forbidden, but do not propagate.

3.3 Particle in a δ-Potential

The Schrödinger equation with an attractive δ-potential

$$V(x) = +V_0\delta(x), \quad V_0 < 0 \tag{3.30}$$

is given by:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_0\delta(x)\right]\psi(x) = E\psi(x). \tag{3.31}$$

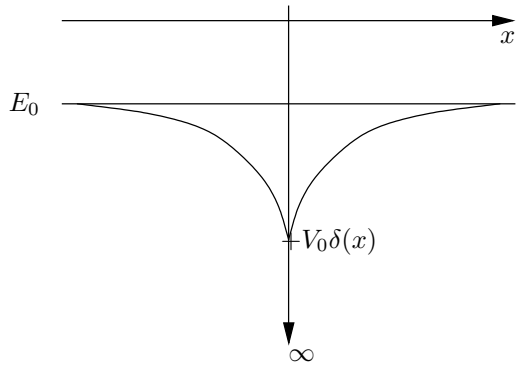

Figure 3.7: Attractive δ-potential

There exist two kinds of solutions, depending on x:

1.) Plane wave or exponential solutions for $x \neq 0$:

$$\psi(x) = \psi_0 e^{ikx} \quad \text{with} \quad k = \pm\frac{\sqrt{2mE}}{\hbar} \tag{3.32}$$

2.) Solution for $x = 0$:
The potential term in the Schrödinger equation has a δ-singularity, which must be compensated by a singularity in $\frac{\partial^2\psi}{\partial x^2}$:

$$-\frac{\hbar^2}{2m}\psi''(x) = -V_0\psi(0)\delta(x) + E\psi(x) \tag{3.33}$$

By integrating the Schrödinger equation over an infinitesimal interval $[-\varepsilon, \varepsilon]$ one gets

$$-\frac{\hbar^2}{2m}[\psi'(\varepsilon) - \psi'(-\varepsilon)] = -V_0\psi(0) + E\underbrace{\int_{-\varepsilon}^{+\varepsilon} dx\psi(x)}_{\to 0 \text{ for } \varepsilon\to 0}. \tag{3.34}$$

Therefore the first derivative has a jump at the origin:

$$\psi'(0^\dagger) - \psi'(0^-) = \frac{2mV_0}{\hbar^2}\psi(0) \tag{3.35}$$

Matching boundary conditions:

1. $E < 0$:

$$k = \pm i\kappa = \pm i\frac{\sqrt{-2mE}}{\hbar} \tag{3.36}$$

$$\psi(x) = \begin{cases} \psi(0)e^{-\kappa x} & , \quad x > 0 \\ \psi(0)e^{+\kappa x} & , \quad x < 0 \end{cases} \tag{3.37}$$

$$\psi'(0^\dagger) - \psi'(0^-) = \psi(0)(-2\kappa) = \frac{2mV_0}{\hbar^2}\psi(0) \tag{3.38}$$

For

$$\kappa = -\frac{mV_0}{\hbar^2} > 0 \tag{3.39}$$

we get a decaying solution for $|x| \to \infty$, i.e. a boundstate, which only exists if the potential is attractive ($V_0 < 0$). For

$$E_0 = -\frac{(\hbar\kappa)^2}{2m} = -\frac{mV_0^2}{2} < 0 \tag{3.40}$$

the boundstate energy is discrete.

2. $E > 0$: Propagating waves (scattering states)

$$k = \pm\frac{\sqrt{2mE}}{\hbar} \tag{3.41}$$

$$\psi(x) = \begin{cases} \psi_0(e^{ikx} + re^{-ikx}) & , \quad x < 0 \\ \psi_0 te^{ikx} + 0 & , \quad x > 0 \end{cases} \tag{3.42}$$

Matching the wave functions at the position $x = 0$ one finds

$$\psi(0^\dagger) = \psi(0^-) \quad \Rightarrow \quad 1 + r = t, \tag{3.43}$$

and for the derivatives

$$\psi'(0^\dagger) - \psi'(0^-) = \frac{2mV_0}{\hbar^2}\psi(0) \tag{3.44}$$

$$\Rightarrow ik(1-r) - ikt = \frac{2mV_0}{\hbar^2}t \tag{3.45}$$

$$ik(1-r) = i(k - i\frac{2mV_0}{\hbar^2})t. \tag{3.46}$$

With $t = 1 + r$ one finally gets

$$r = -\frac{1}{1 + i\frac{\hbar^2 k}{mV_0}} \in \mathbb{C} \tag{3.47}$$

$$t = 1 + r = \frac{i\frac{\hbar^2 k}{mV_0}}{1 + i\frac{\hbar^2 k}{mV_0}}, \quad k = \frac{1}{\hbar}\sqrt{2mE} \tag{3.48}$$

$$|r|^2 + |t|^2 = 1. \tag{3.49}$$

Transmitted and scattered waves suffer a scattering phase shift:

$$|r|^2 = \left(1 + (\frac{\hbar^2}{mV_0})^2 k^2\right)^{-1} \tag{3.50}$$

$$|t|^2 = \left(\frac{\hbar^2}{mV_0}\right)^2 k^2 \cdot \left(1 + (\frac{\hbar^2}{mV_0})^2 k^2\right)^{-1}, \tag{3.51}$$

with the phase shift

$$\delta_r = \frac{\mathrm{Re}(r)}{\mathrm{Im}(r)} = \frac{mV_0}{\hbar^2 k} < 0. \tag{3.52}$$

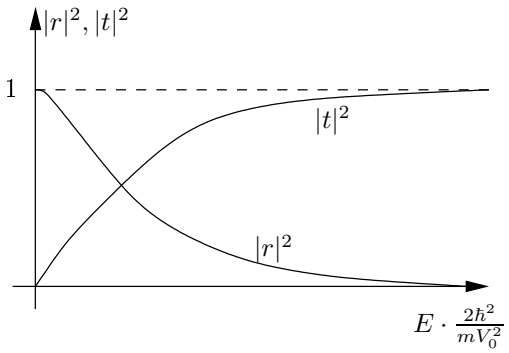

Figure 3.8: Absolute values of the transmission and reflection amplitude

3.4 General theorems in one dimension

1. Energy levels of bound states are always quantized. Propagating states have continuous spectrum.
2. **Node theorem:**
   The number of zeros (nodes) of a wave function increases neccessively with the energy quantum number.

3. There is no degeneracy of energy eigenvalues in one dimension.

Proof:
Let ψ_1, ψ_2 be wave functions with the same energy eigenvalues:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_1}{\partial x^2} + V\psi_1 = E\psi_1 \quad |\cdot\psi_2 \tag{3.53}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_2}{\partial x^2} + V\psi_2 = E\psi_2 \quad |\cdot\psi_1 \tag{3.54}$$

Deriving the difference of the equations (3.53) and (3.54) one finds:

$$\psi_1\frac{\partial^2\psi_2}{\partial x^2} - \psi_2\frac{\partial^2\psi_1}{\partial x^2} = 0 \tag{3.55}$$

$$\Leftrightarrow \frac{\partial}{\partial x}\underbrace{(\psi_1\frac{\partial\psi_2}{\partial x} - \psi_2\frac{\partial\psi_1}{\partial x})}_{=c} = 0 \tag{3.56}$$

Because $\psi_1, \psi_2 \to 0$ for $x \to \infty$ it follows that c has to vanish, i.e. $c = 0$.

$$\frac{1}{\psi_2}d\psi_2 = \frac{1}{\psi_1}d\psi_1 \tag{3.57}$$

$$\Rightarrow \log\psi_2 = \log\psi_1 + d \tag{3.58}$$

$$\Leftrightarrow \psi_2 = e^d\psi_1 \quad \text{equivalent} \tag{3.59}$$

Chapter 4

The Harmonic Oscillator

The Hamiltonian operator for a particle moving in a harmonic potential is given by the expression:

$$H = \frac{p^2}{2m} + V(x) \tag{4.1}$$

with

$$V(x) = 1/2kx^2 = 1/2m\omega^2 x^2, \tag{4.2}$$

wherein ω is the eigenfrequency, $\omega = \sqrt{k/m}$. The importance of the harmonic oscillator in theoretical physics comes clear considering the facts, that

- it is one of the four *exactly solvable* systems.
- it demonstrates, how a solution in quantum mechanics is performed by restricting wave functions to physical Hilbert space (normalizable wave function).
- any bound problem can be represented as a harmonic oscillator for small elongations. Deviations can be treated as perturbation.
- it is even the starting point for quantization of fields.

4.1 Solution in position representation

Stationary Schrödinger equation:

$$H|\psi_E\rangle = E|\psi_E\rangle \tag{4.3}$$

$$\Leftrightarrow \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + 1/2m\omega^2 x^2\right)\psi(x) = E\psi(x) \tag{4.4}$$

The energy eigenvalues E of the harmonic oscillator must be strictly positive.

Proof:
Let $|\psi\rangle$ be an arbitrary eigenstate of H.

$$\langle\psi|H|\psi\rangle = \frac{1}{2m}\langle\psi|\widehat{P}^2|\psi\rangle + 1/2m\omega^2\langle\psi|\widehat{x}^2|\psi\rangle \tag{4.5}$$

$$= \frac{1}{2m}\langle\widehat{P}\psi|\widehat{P}\psi\rangle + 1/2m\omega^2\langle\widehat{x}\psi|\widehat{x}\psi\rangle \tag{4.6}$$

$$> 0 \tag{4.7}$$

In the second step the hermitian property of $\widehat{x}$ and $\widehat{P}$ was used. $|\psi\rangle$ cannot be simultaneously eigenstate of p and x (uncertainty relation).

1. **Dimensionless variables**:
   Characteristic length and energy scales

   $$\Big(\frac{\partial^2}{\partial x^2} + \frac{2m}{\hbar^2}E - \underbrace{\frac{m^2\omega^2}{\hbar^2}}_{1/b^4}x^2\Big)\psi(x) = 0, \tag{4.8}$$

   with the new defined length scale b, $x = by$.

   $$\boxed{b = \sqrt{\tfrac{\hbar}{m\omega}}, \quad \varepsilon = \tfrac{E}{\hbar\omega}} \tag{4.9}$$

   If the partial derivative is described by $\psi'(y) = \frac{\partial\psi}{\partial y}$ etc., one gets

   $$\boxed{\psi''(y) + (2\varepsilon - y^2)\psi(y) = 0}. \tag{4.10}$$

2. **Select physical solutions in Hilbert space**:
   Normalizable to 1 (bound states)

– $y \to \infty$:

$$\psi'' = y^2\psi \tag{4.11}$$

$$\Rightarrow \psi(y) = Ay^m e^{-y^2/2} \tag{4.12}$$

m is an arbitrary but *finite* power. In (4.12) the solution with positive exponent was neglected, because $\psi(y)$ has to vanish exponentiallly for $y \to \pm\infty$.

$$\psi''(y) = Ay^2(y^m + O(y^{m-2}))e^{\pm y^2/2} \tag{4.13}$$

By neglecting the second term proportional to powers $m-2$ of y we found a solution of the differential equation (4.11).

– $y \to 0$:

$$\psi'' + 2\varepsilon\psi = 0 \tag{4.14}$$

$$\Rightarrow \psi(y) = A\cos(\sqrt{2\varepsilon}y) + B\sin(\sqrt{2\varepsilon}y) \tag{4.15}$$

$$= A + \underbrace{B\sqrt{2\varepsilon}}_{C} y + O(y) \tag{4.16}$$

Ansatz:

$$\psi(y) = u(y)e^{-y^2/2} \tag{4.17}$$

with

$$u(y) = A + Cy \quad \text{for } y \to 0, \tag{4.18}$$

$$u(y) = y^m \quad \text{for finite } m \text{ and } y \to \infty. \tag{4.19}$$

$u(y)$ must be a polynomial and of finite order in m to be normalizable. Plugging this into (4.10) one gets:

$$\psi'(y) = u'e^{-y^2/2} - yue^{-y^2/2} \tag{4.20}$$

$$\psi''(y) = u''e^{-y^2/2} - 2yu'e^{-y^2/2} \tag{4.21}$$
$$-ue^{-y^2/2} + y^2ue^{-y^2/2}$$

And by that

$$\boxed{u'' - 2yu' + (2\varepsilon - 1)u = 0}. \tag{4.22}$$

3. **Solution by a power series ansatz**:

$$u(y) = \sum_{n=0}^{m} c_n y^n \quad \text{with } m < \infty \text{ arbitrary} \tag{4.23}$$

Plugging this into equation (4.22) yields:

$$\begin{aligned} 0 &= \sum_{n=0}^{m} c_n[n(n-1)y^{n-2} - 2ny^n \\ &\quad +(2\varepsilon - 1)y^n] \qquad (4.24) \\ \Leftrightarrow 0 &= \sum_{n=0}^{m}[c_{n+2}(n+2)(n+1) \\ &\quad -(2n+1-2\varepsilon)c_n]y^n \qquad (4.25) \end{aligned}$$

It is important to say that in equation (4.24) an index shift has been made. The sum of the second derivative of $u(y)$ starts at $n = 2$. Although it is possible to start the sum at $n = 0$ because the factor $n(n-1)$ lets the first two coefficients vanish. Equation (4.25) must be fulfilled for all y so that we get the recursion relation

$$c_{n+2} = c_n \frac{2n+1-2\varepsilon}{(n+2)(n+1)}. \qquad (4.26)$$

The power series $u(y)$ breaks off at finite m, only if $c_{n+2} = 0$ for some n, i.e

$$\varepsilon_n = n + 1/2 \quad \text{or} \quad \boxed{E_n = (n+1/2)\hbar\omega}. \qquad (4.27)$$

So the energy eigenvalues are quantized due to the normalization.

Now the solutions can be determined by the recursion relation ($y = x/b$):

$$\begin{aligned} E_0 = 1/2\hbar\omega &\Rightarrow H_0(y) = 1 \qquad (4.28) \\ E_1 = (1+1/2)\hbar\omega &\Rightarrow H_1(y) = 2y \qquad (4.29) \\ E_2 = (2+1/2)\hbar\omega &\Rightarrow H_2(y) = -2(1-2y^2) \qquad (4.30) \\ E_3 = (3+1/2)\hbar\omega &\Rightarrow H_3(y) = -12(y - 2/3y^3) \qquad (4.31) \\ E_4 = (4+1/2)\hbar\omega &\Rightarrow H_4(y) = 12(1 - 4y^2 + 4/3y^4) \qquad (4.32) \\ \vdots & \qquad\qquad \vdots \end{aligned}$$

The functions $H_n(y) = H_n(x/b)$ are called *Hermite polynomials.*

– The recursion generates only even or odd polynomials, i.e. eigenfunctions of the parity operator $\widehat{P} : x \mapsto -x$, which commutes with H.

– The normalized eigenfunctions of the harmonic oscillator read

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar 2^{2n}(n!)^2}\right)^{1/4} e^{-\frac{x^2}{2b^2}} H_n(x/b) \tag{4.33}$$

with

$$b = \sqrt{\frac{\hbar}{m\omega}}. \tag{4.34}$$

The normalization constant will be determined below.

– From the algebraic solution results another recursion relation among the Hermite polynomials:

$$H_n'(y) = 2nH_{n-1} \tag{4.35}$$

$$H_{n+1}(y) = 2yH_n - 2nH_{n-1} \tag{4.36}$$

– Orthonormality of eigenfunctions of $\widehat{H}$ for different $n \neq n'$:

$$\int_{-\infty}^{+\infty} H_n(y)H_{n'}(y)e^{-y^2}dy = \delta_{nn'}(\sqrt{\pi}2^n n!) \tag{4.37}$$

with

$$dx = \sqrt{\frac{\hbar}{m\omega}}\, dy. \tag{4.38}$$

– Completeness:

$$\sum \psi_n(x)\psi_n(x') = \delta(x - x') \qquad \text{(algebraic solution)} \tag{4.39}$$

Example:

Construction of the Hermite polynomials and energies ε from the recursion relation, which was given by

$$c_{n+2} = c_n \frac{2n + 1 - 2\varepsilon}{(n+2)(n+1)}. \tag{4.40}$$

– n=0:

From the recursion relation (4.26) we get

$$c_2 = c_0 \frac{2 \cdot 0 + 1 - 2\varepsilon}{2} = 0 \tag{4.41}$$

and we therefore obtain $\varepsilon_0 = 1/2$. The coefficient c_0 is per convention chosen to be 1. Altogether we yield for the first Hermite polynomial and the ground state energy:

$$H_0(y) = 1, \quad E_0 = 1/2\hbar\omega. \tag{4.42}$$

– n=2:

$$\begin{aligned} c_4 &= c_2\frac{5-2\varepsilon}{12} = 0 && (4.43)\\ \Rightarrow \varepsilon_2 &= \frac{5}{2} && (4.44)\\ c_0 &= 1 && (4.45)\\ c_2 &= c_0\frac{1-2\varepsilon}{2} = 1\cdot\frac{1-2\cdot 5/2}{2} = -2 && (4.46)\\ \Rightarrow H_2(y) &= -2(1-2y^2), \quad E_2 = 5/2\hbar\omega && (4.47) \end{aligned}$$

The prefactor -2 is conventional.

– $n = 4$:

$$\begin{aligned} c_6 &= c_4\frac{9-2\varepsilon}{30} = 0 && (4.48)\\ \Rightarrow \varepsilon_4 &= 9/2 && (4.49)\\ c_0 &= 1 && (4.50)\\ c_2 &= c_0\frac{1-2\varepsilon}{2} = \frac{1-2\cdot 9/2}{2} = -4 && (4.51)\\ c_4 &= c_2\frac{5-2\varepsilon}{12} = -4\frac{5-2\cdot 9/2}{12} = 4/3 && (4.52)\\ \Rightarrow H_4(y) &= 12(1-4y^2+4/3y^4), \quad E_4 = 9/2\hbar\omega && (4.53) \end{aligned}$$

Again, the prefactor 12 is conventional.

– $n = 1$:

$$\begin{aligned} c_3 &= c_1\frac{3-2\varepsilon}{6} = 0 && (4.54)\\ \Rightarrow \varepsilon_1 &= 3/2 && (4.55) \end{aligned}$$

The coefficient c_1 is, as before for c_0, per convention chosen to be 1, so that we obtain

$$H_1(y) = 2y, \quad E_1 = 3/2\hbar\omega. \tag{4.56}$$

– $n = 3$:

$$\begin{aligned} c_5 &= c_3\frac{7-2\varepsilon}{20} = 0 && (4.57)\\ \Rightarrow \varepsilon_3 &= 7/2 && (4.58)\\ c_3 &= c_1\frac{3-2\varepsilon}{6} = \frac{3-2\cdot 7/2}{6} = -2/3 && (4.59)\\ \Rightarrow H_3(y) &= -12(y-2/3y^3), \quad E_3 = 7/2\hbar\omega && (4.60) \end{aligned}$$

The prefactor -12 is at least also here conventional.

Properties of the eigenvalue spectrum and the eigenfunctions:

1. The energy eigenvalues $E_n = (n + 1/2)\hbar\omega$ are quantized in units of classical eigenfrequencies.
2. The eigenvalue spectrum is equidistant. This leads to the interpretation of *energy quanta* $\hbar\omega$ as "phonons".
3. All eigenvalues are strictly > 0, as shown initially. The Ground state energy, also called "zero point energy", is given by $E_0 = 1/2\hbar\omega$. The zero point energy greater than zero is a consequence of the fact, that $|\psi\rangle_n$ cannot simultaneously be an eigenstate of $\widehat{p}$ and $\widehat{x}$.

$$\langle\psi_0|H|\psi_0\rangle = \langle\psi_0|\left(\frac{\widehat{p}^2}{2m} + 1/2m\omega\widehat{x}^2\right)|\psi_0\rangle > 0 \tag{4.61}$$

   The zero point energy has the following observable consequences:
   - Vacuum fluctuations, i.e. that the oscillator even contains energy in the ground state.
   - Spontaneous emission of light from an excited atom.
4. The recursion relations generate only purely even or purely odd eigenfunctions $H_n(y)$, i.e. the eigenfunctions of $\widehat{H}$ are parity eigenfunctions. This has to be like that, since the parity operator commutes with $\widehat{H}$, which means that there must exist a simultaneous eigenbasis.
5. Classical turning point of the oscillator for a given energy $E_n = (n + 1/2)\hbar\omega$:

$$\frac{p^2}{2m} = 0 \quad \Rightarrow \quad E_n = 1/2m\omega^2\left(x_{\text{max, class}}\right)^2 \tag{4.62}$$

$$= (n + 1/2)\hbar\omega \tag{4.63}$$

$$\Leftrightarrow x_{\text{max, class}} = \sqrt{n + 1/2}\sqrt{2}\underbrace{\sqrt{\frac{\hbar}{m\omega}}}_{b} \tag{4.64}$$

$$= \sqrt{2n + 1}\cdot b \tag{4.65}$$

   Solutions do not vanish for $x > x_{\text{max, class}}$, but decay exponentially,

$$\psi_n(x) \sim \exp(-\frac{x^2}{2b^2}) = \exp\left(-(n + 1/2)\frac{x^2}{x^2_{\text{class.}}}\right). \tag{4.66}$$

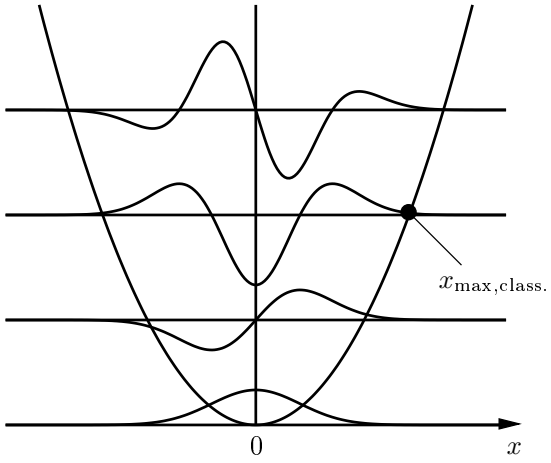

Figure 4.1: Classical and quantum mechancial solutions of the harmonic oscillator

6. Classical limit:
   For $n \to \infty$, the extension into the classically forbidden region vanishes. The wave function oscillates faster and faster. The average $|\psi_n(x)|^2$ corresponds to the classical expectation value. The classical limit will be considered in a separate chapter.

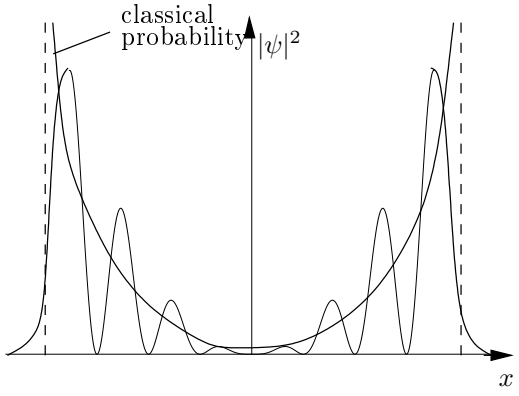

Figure 4.2: Probability density $|\psi(x)|^2$ of a highly excited state

4.2 Harmonic oscillator in the energy eigenbasis: Algebraic solution method

$$H = \frac{1}{2m}\widehat{p}^2 + \frac{1}{2}m\omega^2\widehat{x}^2 \tag{4.67}$$

As will be seen below, for constructing the eigenstate basis of H it is useful, if H can be written in the "factorized" form

$$H = \hbar\omega a^\dagger a + \widetilde{c}_1, \tag{4.68}$$

where $a, c_1 \in \mathbb{R}$ are numbers and $[a, a^\dagger] = \widetilde{c}_2 \in \mathbb{R}$, with $a, a^\dagger$ dimensionless. We construct the appropriate operator a and its hermitian conjugate $a^\dagger$ by completing the square.

$$\begin{aligned}
H &= \text{sum of squares of two operators } \widehat{p}, \widehat{x} && (4.69)\\
a &= \alpha\widehat{x} + i\beta\widehat{p}, \qquad \alpha,\, \beta \in \mathbb{R} && (4.70)\\
a^\dagger &= \alpha\widehat{x} - i\beta\widehat{p} && (4.71)\\
\left[a, a^\dagger\right] &= -2i\alpha\beta[\widehat{x}, \widehat{p}] = +2\alpha\beta\hbar && (4.72)\\
a^\dagger a &= \alpha^2\widehat{x}^2 + \beta^2\widehat{p}^2 + i\alpha\beta\widehat{x}\widehat{p} - i\alpha\beta\widehat{p}\widehat{x} && (4.73)\\
&= \alpha^2\widehat{x}^2 + \beta^2\widehat{p}^2 + i\alpha\beta[\widehat{x}, \widehat{p}] && (4.74)\\
&= \alpha^2\widehat{x}^2 + \beta^2\widehat{p}^2 - \hbar\alpha\beta && (4.75)\\
\hbar\omega a^\dagger a &\stackrel{!}{=} \frac{\widehat{p}^2}{2m} + \frac{1}{2}m\omega^2\widehat{x}^2 - \widetilde{c}_1 && (4.76)
\end{aligned}$$

By comparison we obtain:

$$\begin{aligned}
\alpha^2\hbar\omega &= \frac{1}{2}m\omega^2 \quad \Leftrightarrow \quad \alpha = \sqrt{\frac{m\omega}{2\hbar}} = \frac{1}{\sqrt{2}b} && (4.77)\\
\beta^2\hbar\omega &= \frac{1}{2m} \quad \Leftrightarrow \quad \beta = \sqrt{\frac{1}{2m\hbar\omega}} && (4.78)\\
\hbar\alpha\beta &= \widetilde{c}_1 = \frac{1}{2} && (4.79)
\end{aligned}$$

And hence:

$$\boxed{\begin{aligned} a &= \sqrt{\frac{m\omega}{2\hbar}}\widehat{x} + i\sqrt{\frac{1}{2m\hbar\omega}}\widehat{p} \\ a^\dagger &= \sqrt{\frac{m\omega}{2\hbar}}\widehat{x} - i\sqrt{\frac{1}{2m\hbar\omega}}\widehat{p} \\ H &= \hbar\omega\left[a^\dagger a + \frac{1}{2}\right] \\ \left[a, a^\dagger\right] &= 1 \end{aligned}} \tag{4.80}$$

The term $1/2\hbar\omega$ in the Hamilton operator is the zero-point energy. Up to now we have just rewritten the original harmonic oscillator hamiltonian H in a factorized form by "completing the square", where the "factorizing" operators $a, a^\dagger$ have the *canonical* commutation relation $[a, a^\dagger] = 1$. Note that this is possible, precisely, because

- H is a quadratic form,
- in the canonically conjugate operators $\widehat{x}$, $\widehat{p}$: $[\widehat{x}, \widehat{p}] = i\hbar$,
- with positive coefficients,

i.e. only for the harmonic oscillator. The factorization of H in terms of canonical operators $[a, a^\dagger] = 1$ (real) makes the harmonic oscillator unique and of central importance for field quantization.

Construction of the eigenstates in terms of a, $a^\dagger$:
However, we have not diagonalized H yet. The crucial insight is gained by recognizing that the eigenstates $|n\rangle$ of the harmonic oscillator can be constructed from a, $a^\dagger$, using $[a, a^\dagger] = 1$:

Let $|n\rangle$ be an eigenstate of H with the energy $E_n = (n + 1/2)\hbar\omega$:

$$H|n\rangle = E_n|n\rangle \tag{4.81}$$

with

$$H = \hbar\omega(a^\dagger a + 1/2). \tag{4.82}$$

Then:

$$\begin{aligned}
\hbar\omega(a^\dagger a + 1/2)a^\dagger|n\rangle &= \hbar\omega a^\dagger(a^\dagger a + 3/2)|n\rangle && (4.83)\\
&= \hbar\omega(n+3/2)a^\dagger|n\rangle && (4.84)\\
&= (\underbrace{E_n + \hbar\omega}_{E_{n+1}})a^\dagger|n\rangle && (4.85)\\
\Leftrightarrow a^\dagger|n\rangle &= c_{n+1}|n+1\rangle && (4.86)
\end{aligned}$$

This is a not normalized eigenstate with energy

$$E_{n+1} = E_n + \hbar\omega = \hbar\omega[(n+1) + 1/2]. \quad (4.87)$$

Analogously:

$$\begin{aligned}
\hbar\omega(a^\dagger a + 1/2)a|n\rangle &= \hbar\omega a(a^\dagger a - 1/2)|n\rangle && (4.88)\\
&= \hbar\omega(n-1/2)a|n\rangle && (4.89)\\
&= E_{n-1}a|n\rangle && (4.90)\\
\Leftrightarrow a|n\rangle &= \widetilde{c}_n|n-1\rangle && (4.91)
\end{aligned}$$

This is a not normalized eigenstate with energy E_{n-1}. Therefore $a^\dagger, a$ are called raising and lowering operators. Since all eigenvalues of H are $E_n > 0$ (see section 4.1), the lowering chain must break off at some n_0:

$$\begin{aligned}
a|n\rangle &= 0 && (4.92)\\
\hbar\omega(a^\dagger a + 1/2)|n_0\rangle &= 1/2\hbar\omega|n_0\rangle && (4.93)
\end{aligned}$$

That means:

$$\begin{aligned}
E_{n_0} &= E_0 && (4.94)\\
|n_0\rangle &= |n=0\rangle && (4.95)
\end{aligned}$$

The ground state $|0\rangle$ is annihilated by a. *All* excited states are generated by $a^\dagger$ acting repeatedly on $|0\rangle$.

Proof:
Consider *any* eigenstate $|\widetilde{n}\rangle$ with eigenenergy $E_{\widetilde{n}}$, which is not necessarily contained in the family of eigenstates $\mathbb{B} = \{(a^\dagger)^n|0\rangle|n = 0, 1, 2, \ldots\}$. It

can be lowered to a state of minimal energy, the ground state, by repeated action of a. Since the ground state is unique (e.g. no degeneracy in $d = 1$), $|\widetilde{n}\rangle$ must be a member of $\mathbb{B}$.

Computation of the matrix elements of a, $a^\dagger$ in the energy eigenbasis:

$$\begin{aligned}
a|n\rangle &= c_n|n-1\rangle && (4.96)\\
\langle n|a^\dagger a|n\rangle &= c_n^* c_n \underbrace{\langle n-1|n-1\rangle}_{=1 \text{ (normalized)}} = |c_n|^2 && (4.97)\\
\Leftrightarrow \langle n|\frac{H}{\hbar\omega} - \frac{1}{2}|n\rangle &= |c_n|^2 && (4.98)\\
\Leftrightarrow n &= |c_n|^2 && (4.99)\\
\Leftrightarrow c_n &= \sqrt{n}e^{i\Phi} \quad \text{(usually define } \Phi = 0) && (4.100)
\end{aligned}$$

The annihilation condition

$$a|0\rangle = 0 \cdot |-1\rangle \tag{4.101}$$

is fulfilled. Now consider the raising operator $a^\dagger$.

$$\begin{aligned}
a^\dagger|n\rangle &= c_{n+1}|n\rangle && (4.102)\\
\langle n|aa^\dagger|n\rangle &= |c_{n+1}|^2 && (4.103)\\
\Leftrightarrow \langle n|1 + a^\dagger a|n\rangle &= |c_{n+1}|^2 && (4.104)\\
\Leftrightarrow \langle n|1 + (\frac{H}{\hbar\omega} - \frac{1}{2})|n\rangle &= |c_{n+1}|^2 && (4.105)\\
\Leftrightarrow n+1 &= |c_{n+1}|^2 && (4.106)\\
\Leftrightarrow c_{n+1} &= \sqrt{n+1}e^{i\Phi} && (4.107)
\end{aligned}$$

$$\boxed{\begin{aligned}
a|n\rangle &= \sqrt{n}|n-1\rangle\\
a^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle\\
a^\dagger a|n\rangle &= n|n\rangle
\end{aligned}} \tag{4.108}$$

Rule: The factor under the square root is always the larger quantum number appearing in the equation.

Example:
In the energy eigenbasis

$$|n\rangle = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} \tag{4.109}$$

$$a = \begin{pmatrix} 0 & \sqrt{1} & & & & \\ & 0 & \sqrt{2} & & & \\ & & 0 & \sqrt{3} & & \\ & & & \ddots & \ddots & \\ & & & & \ddots & \ddots \\ 0 & & & & & 0 \end{pmatrix} \tag{4.110}$$

$$a^\dagger = \begin{pmatrix} 0 & 0 & & & & \\ \sqrt{1} & 0 & 0 & & & \\ & \sqrt{2} & 0 & 0 & & \\ & & \sqrt{3} & 0 & 0 & \\ & & & \ddots & \ddots & \ddots \\ 0 & & & & & 0 \end{pmatrix} \tag{4.111}$$

The above relations enable us to calculate *any* physical expectation value of an observable Ω in the oscillator.

$$\Omega = \Omega(\widehat{x}, \widehat{p}) \qquad \text{(defined as power series in } \widehat{x}, \widehat{p}) \tag{4.112}$$

$$\widehat{x} = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger) \tag{4.113}$$

$$\widehat{p} = i\sqrt{\frac{m\omega\hbar}{2}}(a^\dagger - a) \tag{4.114}$$

For example

$$\langle n|\widehat{x}^2|n\rangle, \ \langle n|\widehat{p}^2|n\rangle. \tag{4.115}$$

Interpretation:
The operators a, $a^\dagger$ are due to their action called

– ladder,

– raising and lowering or

– creation and annihilation

operators.

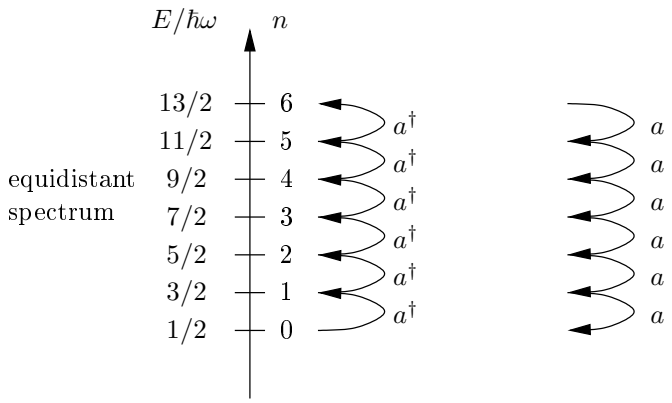

Figure 4.3: Visualization of the ladder operators

$a^\dagger$ (a) increases (reduces) the excitation state of the system by one unit $\hbar\omega$. It can be seen as adding (removing) one *energy quantum* $\hbar\omega$ to (from) the oscillator. Therefore $a^\dagger$ (a) are called creation (destruction) operator of an energy quantum $\hbar\omega$ of the oscillator. The energy quantum $\hbar\omega$ is often called "phonon", in reminiscence of the oscillation like in a sound wave. This quantized energy packet can be interpreted as a particle - like photons in an electromagnetic wave (oscillation). An oscillator in excitation state n is said to contain n phonons.

$$N = a^\dagger a = \text{phonon number operator} \tag{4.116}$$

Outlook to field quantization:
Consider a harmonic lattice like it is shown in figure 4.4:

The harmonic potential between neighboring lattice points reads

$$V(x_0 \dots x_N) = \sum_{i=0}^{N} 1/2 m\omega^2 (x_i - x_{i+1} - x_{i-1})^2, \tag{4.117}$$

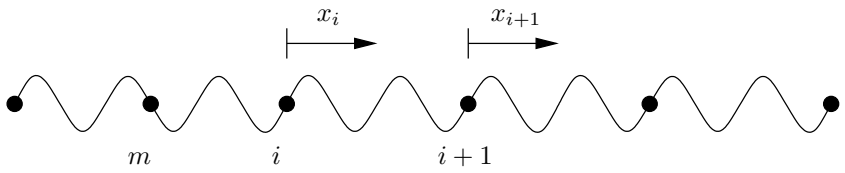

Figure 4.4: Harmonic lattice

with the periodic boundary conditions

$$-1 = N, \quad N + 1 = 1. \tag{4.118}$$

The kinetic term is given by

$$T = \sum_{i=0}^{N} \frac{1}{2m} p_i^2 \tag{4.119}$$

and the Hamiltonian therefore by

$$H = T + V. \tag{4.120}$$

The system of coupled harmonic oscillators can be decoupled by a transformation to normal modes. The energy quanta of the harmonic oscillators represented by the normal modes are called phonons in solid state physics. In this way the *field* of harmonic oscillators (one oscillator at each lattice point) is *quantized*.

Direct computation of the harmonic oscillator eigenfunctions in the x basis (Hermite polynomials):

1. Ground state: $a|0\rangle = 0$

$$\begin{aligned} a &= \sqrt{\frac{m\omega}{2\hbar}}\widehat{x} + i\sqrt{\frac{1}{2m\omega\hbar}}\widehat{p} && (4.121)\\ &= \frac{1}{\sqrt{2}} y + i\sqrt{\frac{1}{2m\omega\hbar}}\left(-i\hbar\frac{d}{dx}\right) && (4.122)\\ &= \frac{1}{\sqrt{2}} y + i\sqrt{\frac{1}{2m\omega\hbar}}\left(-i\sqrt{m\omega\hbar}\frac{d}{dy}\right) && (4.123)\\ &= \frac{1}{\sqrt{2}}\left(y + \frac{d}{dy}\right) && (4.124)\\ a^\dagger &= \frac{1}{\sqrt{2}}\left(y - \frac{d}{dy}\right) && (4.125) \end{aligned}$$

In position basis one gets a differential equation for ψ_0:

$$\begin{aligned}
\left(y + \frac{d}{dy}\right)\Psi_0(y) &= 0 && (4.126)\\
\Leftrightarrow \frac{d\psi_0}{\psi_0} &= -y\,dy && (4.127)\\
\Leftrightarrow \ln\psi_0'|_{\psi_0^0}^{\psi_0} &= -1/2y^2 && (4.128)\\
\Leftrightarrow \psi_0(y) &= A_0 e^{-y^2/2} && (4.129)\\
\Leftrightarrow \psi_0(x) &= A_0 \exp\left(-\frac{m\omega x^2}{2\hbar}\right), && (4.130)
\end{aligned}$$

with the normalization factor A_0 of the Gaussian

$$A_0 = \sqrt{\frac{m\omega}{\pi\hbar}}^{1/2} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}. \qquad (4.131)$$

2. All excited wave functions can be generated from $\psi_0(x)$ by operating $(a^\dagger)^n = \left[\frac{1}{\sqrt{2}}\left(y - \frac{d}{dy}\right)\right]^n$ on $\psi_0(y)$:

$$\psi_n(y) = A_n\left[\frac{1}{\sqrt{2}}\left(y - \frac{d}{dy}\right)\right]^n \psi_0(y), \qquad y = \frac{x}{b} \qquad (4.132)$$

The operator $(y - \frac{d}{dy})$ generates the Hermite polynomials with the above conventional prefactors.

3. Normalization factor A_n:

a) $n = 0$:

$$1 = \int dx\, \psi_0^2(x) \tag{4.133}$$

$$= A_0^2 \int dx\, e^{-\frac{m\omega}{\hbar}x^2} = A_0^2 \int dx\, e^{-\frac{x^2}{b^2}} \tag{4.134}$$

$$= A_0^2 \int_{-\infty}^{+\infty} dy \sqrt{\frac{\hbar}{m\omega}} e^{-y^2} \tag{4.135}$$

$$= A_0^2 \sqrt{\frac{\hbar}{m\omega}} \left[\int_{-\infty}^{+\infty} \int dx\, dy\, e^{-(x^2+y^2)} \right]^{1/2} \tag{4.136}$$

$$= A_0^2 \sqrt{\frac{\hbar}{m\omega}} \left[2\pi \int_0^{\infty} dr\, r e^{-r^2} \right]^{1/2} \tag{4.137}$$

$$= A_0^2 \sqrt{\frac{\hbar}{m\omega}} \left[2\pi \int_0^{\infty} dr \left(-\frac{1}{2}\frac{d}{dr} e^{-r^2} \right) \right]^{1/2} \tag{4.138}$$

$$= A_0^2 \sqrt{\frac{\pi\hbar}{m\omega}} \tag{4.139}$$

$$\Leftrightarrow A_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \tag{4.140}$$

– $n > 0$:

We know that the operator

$$\frac{1}{\sqrt{n!}}(a^\dagger)^n = \frac{1}{\sqrt{n!}}\frac{1}{\sqrt{2}^n}\left[\left(y - \frac{d}{dy}\right)\right]^n \tag{4.141}$$

acting on $|0\rangle$ generates the normalized eigenstates, and that $\left(y - \frac{d}{dy}\right)^n$ by convention generates $H_n(y)$ (unnormalized).

$$A_n = \frac{1}{\sqrt{n!}}\frac{1}{2^{n/2}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} = \left(\frac{m\omega}{\pi\hbar 2^{2n}(n!)^2}\right)^{1/4} \tag{4.142}$$

4. The recursion for $H_n(y)$ can be achieved from the a, $a^\dagger$ algebra in a similar way.

4.3 Coherent states

We now construct the eigenstates of the destruction operator a. Clearly, these states cannot be energy eigenstates, unless the eigenvalue is the trivial one, since a changes the energy quantum number n. However, as we shall see, the eigenstates of a are of importance, because

- their x, p expectation values obey the classical motion.
- they form wave packets, which do not run apart as time increases (no dispersion).

They are called "coherent states" and are important in laser physics and quantum optics. Eigenstates of a:

$$a|\varphi_\alpha\rangle = \alpha|\varphi_\alpha\rangle, \qquad \alpha \in \mathbb{C} \text{ eigenvalue } (a \text{ not hermitean!}) \tag{4.143}$$

Expansion in energy eigenstates:

$$|\varphi_\alpha\rangle = \sum_{n=0}^{\infty} \varphi_{\alpha n}|n\rangle, \tag{4.144}$$

with:

$$\begin{aligned}
\varphi_{\alpha n} &= \langle n|\varphi_\alpha\rangle && (4.145)\\
&= \frac{1}{\sqrt{n!}}\langle 0|a^n|\varphi_\alpha\rangle && (4.146)\\
&= \frac{\alpha^n}{\sqrt{n!}}\langle 0|\varphi_\alpha\rangle = \frac{\alpha^n}{\sqrt{n!}}\varphi_{\alpha 0} && (4.147)\\
\Rightarrow |\varphi_\alpha\rangle &= \varphi_{\alpha 0}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|n\rangle && (4.148)\\
&= \varphi_{\alpha 0}\sum_{n=0}^{\infty}\frac{(\alpha a^\dagger)^n}{n!}|0\rangle && (4.149)\\
&= \varphi_{\alpha 0}e^{\alpha a^\dagger}|0\rangle && (4.150)
\end{aligned}$$

The normalization yields:

$$\begin{aligned}
1 &= \langle\varphi_\alpha|\varphi_\alpha\rangle = |\varphi_{\alpha 0}|^2\sum_{n=0}^{\infty}\frac{|\alpha|^{2n}}{n!} = |\varphi_{\alpha 0}|^2 e^{|\alpha|^2} && (4.151)\\
\Leftrightarrow |\varphi_{\alpha 0}| &= e^{-|\alpha|^2/2}, \qquad \alpha \in \mathbb{C} \text{ arbitrary.} && (4.152)
\end{aligned}$$

Position representation of the coherent states; time evolution:

$$\psi_n(x,t) = \langle x|n\rangle = \psi_n(x)e^{-i\frac{E_n t}{\hbar}}, \tag{4.153}$$

the t-dependent energy eigenstates with eigenvalues

$$E_n = \hbar\omega(n+1/2). \tag{4.154}$$

Position representation of the coherent states:

$$\varphi_\alpha(x,t) = \langle x|\varphi_\alpha\rangle \tag{4.155}$$

$$= e^{-1/2|\alpha|^2}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}\psi_n(x)e^{-i\omega(n+1/2)t} \tag{4.156}$$

$$= e^{-1/2|\alpha|^2}\sum_{n=0}^{\infty}\frac{\overbrace{(\alpha e^{-i\omega t})^n}^{\alpha(t)}}{\sqrt{n!}}\psi_n(x)e^{-i\omega t/2} \tag{4.157}$$

One obtains the coherent wave function

$$\boxed{\varphi_\alpha(x,t) = \varphi_{\alpha(t)}(x)e^{-i\omega t/2}} \tag{4.158}$$

with

$$\alpha(t) = \alpha(0)e^{-i\omega t}, \quad \alpha(0) = |\alpha|e^{i\delta} \tag{4.159}$$

and the following properties:

– the t-dependence is that of a t-dependent $\alpha(t)$ and a trivial phase $e^{-i\omega t}$. The x expectation value of a particle in a state φ_α reads:

$$\langle x\rangle = \langle\varphi_\alpha(t)|x|\varphi_\alpha(t)\rangle \tag{4.160}$$

$$= \langle\varphi_\alpha(t)|\frac{b}{\sqrt{2}}(a+a^\dagger)|\varphi_\alpha(t)\rangle, \quad b=\sqrt{\frac{\hbar}{m\omega}} \tag{4.161}$$

$$= \frac{b}{\sqrt{2}}(\alpha(t)+\alpha^*(t)) \tag{4.162}$$

$$= \sqrt{2}b|\alpha|\cos(\omega t-\delta) \tag{4.163}$$

$$= \langle x(t)\rangle \tag{4.164}$$

– The x dependence is given by

$$|\varphi_\alpha(x,t)|^2 = \frac{1}{\sqrt{\pi}b}\exp\left(-\frac{(x-\sqrt{2}|\alpha|b\cos(\omega t-\delta))^2}{b^2}\right), \tag{4.165}$$

which represents an oscillating Gaussian wave packet without dispersion and is therefore coherent.

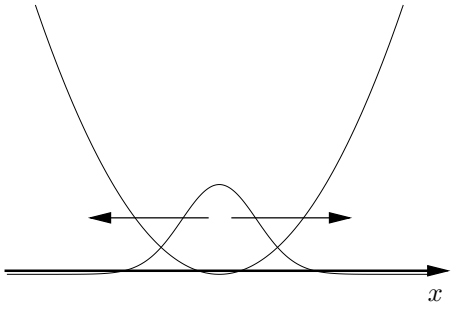

Figure 4.5: Gaussian wave paket without dispersion

Chapter 5

Path integral formulation of quantum theory

In this chapter we develop another formulation of the quantum theory, which is equivalent to the Schrödinger formulation, but allows a more fundamental understanding of the Schrödinger equation as well as of the correction to classical mechanics.

5.1 The propagator $U(\vec{x}, t; \vec{x}\,', 0)$

Since the Schrödinger equation is of first order in time, its solution at any instant of time t, $\psi(\vec{x}, t)$, is uniquely determined once the state, in x representation the wave function, is fixed at a time t', $\psi(\vec{x}, t' = 0)$. Without loss of generality we set $t' = 0$ in the following. This can be expressed formally for H not explicitly t-dependent.

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}Ht}|\psi(0)\rangle \qquad \text{(basis-free representation)}, \tag{5.1}$$

since

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = He^{-\frac{i}{\hbar}Ht}|\psi(0)\rangle = H|\psi(t)\rangle \quad \text{(Schrödinger equation)}. \tag{5.2}$$

The operator $U(t) = e^{-\frac{i}{\hbar}Ht}$ depends only on the system H, not on the initial condition $|\psi(0)\rangle$. It is called *time evolution operator* or *propagator* of the system.

– **In energy representation:**
$\{|n\rangle\}$ basis of eigenstates of H with eigenvalues E_n

$$|\psi(t)\rangle = \sum_n e^{-\frac{i}{\hbar}Ht}|n\rangle\langle n|\psi(0)\rangle \tag{5.3}$$

$$= \sum_n |n\rangle\langle n|\psi(0)\rangle e^{-\frac{i}{\hbar}E_n t} \tag{5.4}$$

$$U(t) = \sum_n |n\rangle\langle n|e^{-\frac{i}{\hbar}E_n t} \tag{5.5}$$

– **In position representation:**

$$\langle\vec{x}|\psi(t)\rangle = \int d^3x' \underbrace{\langle\vec{x}|e^{-\frac{i}{\hbar}Ht}|\vec{x}'\rangle}_{U(\vec{x},t;\vec{x}',0)}\langle\vec{x}'|\psi(0)\rangle \tag{5.6}$$

$$\psi(\vec{x},t) = \int d^3x' U(\vec{x},t;\vec{x}',0)\psi(\vec{x}',0) \tag{5.7}$$

$U(t) = e^{-\frac{i}{\hbar}Ht}$ obeys the differential equation

$$i\hbar\frac{\partial}{\partial t}U = HU, \tag{5.8}$$

i.e. the Schrödinger equation. However, it is an *operator* acting on Hilbertspace, not a vector. All information about the system can be extracted from the propagator $U(t)$. Instead of solving the Schrödinger, one can formulate the quantum theory based on a direct calculation of the propagator, without resorting to the Schrödinger equation.

5.2 Formulation of the path integral

Based on very general considerations[1] we develop the scheme how to calculate $U(\vec{x},t;\vec{x}',0)$ in position representation:

1. **Interpretation of the propagator equation:**
$U(\vec{x},t;\vec{x}',0)$ is the *amplitude* for finding the particle at time t at $\vec{x}$,

[1]The formulation is based on the concept of a particle which propagates from one position to another according to probability amplitudes, i.e. is in the spirit of the Copenhagen statistical interpretation of the quantum theory. However this formulation does not preassume a Schrödinger equation or any other dynamical equation.

provided it has been (or will be) at time $t' = 0$ at $\vec{x}'$. Since $\psi(\vec{x}', 0)$ is the *amplitude* that at $t' = 0$ the particle has been at $\vec{x}'$, one must integrate the propagator equation over all possible $\vec{x}'$ in order to get the total amplitude $\psi(\vec{x}, t)$ of finding the particle at $(\vec{x}, t)$.

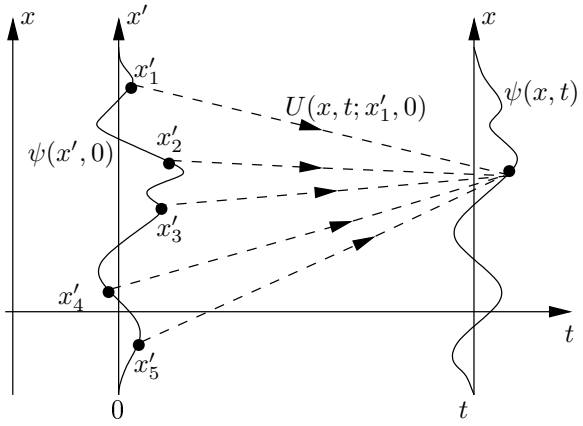

Figure 5.1: Visualization of the propagator U between two states $\psi(x', 0)$ and $\psi(x, t)$

2. **Ansatz for $U(\vec{x}, t; \vec{x}', 0)$:**
   How can we calculate this amplitude $U(\vec{x}, t; \vec{x}', 0)$, i.e. how does the particle move from $(\vec{x}', 0)$ to $(\vec{x}, t)$? Without knowing anything about the dynamics, the *minimal* assumption is that the particle can move on *any* path $\vec{x}(t)$ from $(\vec{x}', 0)$ to $(\vec{x}, t)$ with *equal probability*, $|W\{\vec{x}(\widetilde{t})\}|^2 = 1$. Then the only possible choice for the amplitude $W\{\vec{x}(\widetilde{t})\}$ is a phase factor, $W\{\vec{x}(\widetilde{t})\} = e^{-i\phi\{\vec{x}(t)\}}$, and to get the total amplitude $U(\vec{x}, t; \vec{x}', 0)$ we have to sum up *all* the amplitudes of paths $\vec{x}(t)$ which begin at $(\vec{x}', 0)$ and end at $(\vec{x}, t)$:

$$\boxed{U(\vec{x}, t; \vec{x}', 0) = A \sum_{\substack{\text{paths}\,\vec{x}(\widetilde{t}) \\ \vec{x}(0)=\vec{x}' \\ \vec{x}(t)=\vec{x}}} e^{+i\phi\{\vec{x}(\widetilde{t})\}}}, \tag{5.9}$$

   where A is a normalization factor.

3. **Choice of the phase $\phi\{\vec{x}(\widetilde{t})\}$ attributed to a path $\vec{x}(\widetilde{t})$:**
   The only known requirement on $W\{\vec{x}(\widetilde{t})\}$ is that for a classical particle (large mass, action $S \gg \hbar$) only the classical path $\vec{x}_{\text{cl}}(\widetilde{t})$ should contribute to $U(\vec{x}, t; \vec{x}', 0)$. Therefore we choose

$$W\{\vec{x}(\widetilde{t})\} = e^{+\frac{i}{\hbar} S\{\vec{x}(\widetilde{t})\}}, \tag{5.10}$$

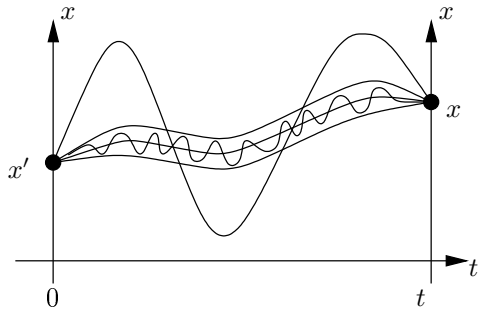

Figure 5.2:

i.e. the actions of the path $\vec{x}(\widetilde{t})$ in units of $\hbar$. The weight factor W is oscillatory as a function of S. Contributions W from different paths have in general an arbitrary relative phase $S/\hbar = \phi\{\vec{x}(\widetilde{t})\}$. In the summation over all paths the contributions, therefore, cancel each other in general. However, for the classical path $x_{\rm cl}(t)$ the action is stationary (stationary phase)[2]:

$$\delta S\{\vec{x}(t)\}\Big|_{\vec{x}(t)=x_{\rm cl}(t)} = 0 \tag{5.11}$$

$$S\{\vec{x},\dot{\vec{x}}\} = \int_0^t d\widetilde{t}\,[\frac{1}{2}m\dot{\vec{x}}^2(\widetilde{t}) - V(\vec{x}(\widetilde{t}))] \tag{5.12}$$

Hence, only the contributions from paths close to the classical path interfere constructively. The range of constructive interference is roughly

$$|S\{\vec{x}(t)\} - S\{\vec{x}_{\rm cl}(t)\}| \leq \pi \qquad \text{(region of coherence)}. \tag{5.13}$$

For large mass (or excitation energy), S varies rapidly as $x(t)$ is varied from the classical path $x_{\rm cl}(t)$, and in the limit $S \gg \hbar$ (classical limit) only the classical path contributes.

Example: Free particle

$$x_{\rm cl}(t) = vt, \quad v = \frac{x_1}{t_1} \tag{5.14}$$

$$x_1(t) = \frac{1}{2}at^2, \quad a = \frac{2x_1}{t_1^2} \tag{5.15}$$

$$x_1(0) = x_{\rm cl}(0) = 0 \tag{5.16}$$

$$x_1(t_1) = x_{\rm cl}(t_1) = x_1 \tag{5.17}$$

[2]From equation (5.11) one can obtain the Euler-Lagrange equations ($\rightarrow$ variation principle).

Action:

$$S_{\rm cl} = \int_0^{t_1} dt\, 1/2m\dot{x}_{cl}^2 \tag{5.18}$$

$$= \int_0^{t_1} dt\, 1/2mv^2 = 1/2m\frac{x_1^2}{t_1} \tag{5.19}$$

$$S_1 = \int_0^{t_1} dt\, 1/2m\dot{x_1}^2 \tag{5.20}$$

$$= \int_0^{t_1} dt\, 1/2ma^2t^2 = 2/3m\frac{x_1^2}{t_1} > S_{\rm cl} \tag{5.21}$$

$$\Rightarrow S_1 - S_{cl} = 1/6m\frac{x_1^2}{t_1} \tag{5.22}$$

$$\approx 10^{27}\hbar, \tag{5.23}$$

which is valid for macroscopic parameters. We have deduced the scheme to calculate the quantum mechanical time evolution operator, which contains the classical Lagrangean formalism, $\delta S = 0$ for $x_{\rm cl}$, in a natural way for $S \gg \hbar$. This construction also offers an approximation scheme:

→ Quasiclassical approximation

→ Expansion about x_{cl}

→ Stationary phase approximation

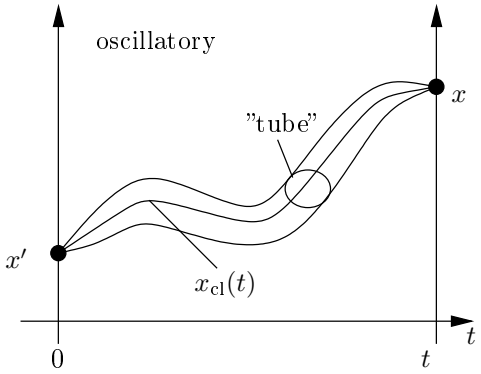

Figure 5.3: "Tube" around $x_{\rm cl}(t)$ within which $S - S_{\rm cl} \leq \pi$

$$\boxed{U(\vec{x},t;\vec{x}\,',0) = \int_{x(0)=x'}^{x(t)=x} \mathfrak{D}\{x(\widetilde{t})\} e^{+\frac{i}{\hbar}S\{\vec{x}(\widetilde{t})\}}} \tag{5.24}$$

5.3 Evaluation of the path integral for a free particle: the measure

We restrict ourselves to the one-dimensional case, i.e. $d = 1$. To perform the summation over the continuous set of all paths $x(t)$, we first discretize the paths into $(N+1)-$time slices of spacing $\varepsilon = \frac{t}{N}$ and evaluate the limits $N \to \infty$ and $\varepsilon \to 0$ at the end of the calculation.

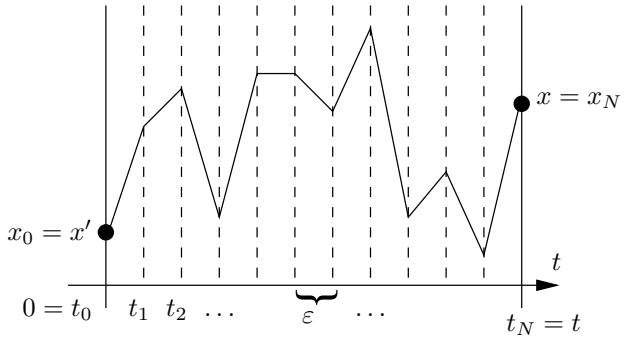

Figure 5.4: Discretizing the paths into $(N+1)-$times slices of spacing ε

$$
\begin{aligned}
U(x,t;x',0) &= \lim_{N\to\infty} A_N \int dx_1 \int dx_2 \\
&\quad \ldots \int dx_{N-1} \exp\left(+\frac{i}{\hbar} S\{x(t)\}\right) && (5.25)\\
&= \int \mathfrak{D}\{x(t)\}\, e^{+\frac{i}{\hbar}S\{x(t)\}} && (5.26)\\
S\{x(t)\} &= \sum_{i=0}^{N-1} 1/2m \left(\frac{x_{i+1}-x_i}{\varepsilon}\right)^2 \cdot \varepsilon && (5.27)\\
&\underset{\varepsilon=dt\to 0}{\longrightarrow} \int dt\, 1/2m \left(\frac{dx}{dt}\right)^2, && (5.28)
\end{aligned}
$$

where $x_0 = x'$ and $x_N = x$ are fixed under the path of the integral. The integrals over x_i are quadratic and, hence, can be performed.

Substitute dimensionless integration variables:

$$y_i = \sqrt{\frac{m}{2\hbar\varepsilon}}x_i, \quad i = 1, \ldots, N-1 \tag{5.29}$$

$$\begin{aligned} U(x,t;x',0) &= \lim_{N\to\infty} A_N \left(\frac{2\hbar\varepsilon}{m}\right)^{(N-1)/2} \int dy_1 \ldots \\ &\quad \times \int dy_{N-1} \exp\left(i\sum_{i=0}^{N-1}(y_{i+1}-y_i)^2\right) \end{aligned} \tag{5.30}$$

The integration over y_1 yields:

$$\int dy_1 \exp\left(-\frac{1}{i}\left[(y_1-y_0)^2+(y_2-y_1)^2\right]\right) \tag{5.31}$$

$$= \int dy_1 \exp\left(-\frac{1}{i}\left[2\left(y_1-\frac{y_0+y_2}{2}\right)^2+\frac{1}{2}(y_2-y_0)^2\right]\right) \tag{5.32}$$

$$= \sqrt{\frac{i\pi}{2}}\exp\left(-\frac{1}{i}\frac{(y_2-y_0)^2}{2}\right) \tag{5.33}$$

The Gaussian form is reproduced, with y_1 removed and an additional factor $\frac{1}{2}$. Moreover the integration over y_2 gives:

$$\left(\frac{i\pi}{2}\right)^{1/2}\int dy_2 \exp\Big(-\frac{1}{i}[1/2(y_2-y_0)^2+(y_3-y_2)^2]\Big) \tag{5.34}$$

$$= \left(\frac{i\pi}{2}\right)^{1/2}\left(\frac{2\pi i}{3}\right)^{1/2}\exp\left(-\frac{1}{i}\frac{(y_3-y_0)^2}{3}\right) \tag{5.35}$$

$$= \sqrt{\frac{(i\pi)^2}{3}}\exp\left(-\frac{1}{i}\frac{(y_3-y_0)^2}{3}\right) \tag{5.36}$$

Performing all $N-1$ integrals finally gives:

$$\begin{aligned} U(x,t;x',0) &= \lim_{N\to\infty} A_N \left(\frac{2\hbar\varepsilon}{m}\right)^{\frac{N-1}{2}} \left(\frac{(i\pi)^{N-1}}{N}\right)^{1/2} \\ &\quad \times \exp\left(-\frac{1}{i}(y_N-y_0)^2/N\right) \end{aligned} \tag{5.37}$$

$$\begin{aligned} &= \lim_{N\to\infty} A_N \left(\frac{2\pi\hbar\varepsilon i}{m}\right)^{\frac{N}{2}} \left(\frac{m}{2\pi i\hbar N\varepsilon}\right)^{1/2} \\ &\quad \times \exp\left(i\frac{m}{2\hbar N\varepsilon}(x-x_1)^2\right) \end{aligned} \tag{5.38}$$

To get a well-defined result for $N \to \infty$ and $\varepsilon = t/N \to 0$ the N-dependence must be canceled by the factor A_N ($(t/N)^N \underset{N\to\infty}{\longrightarrow} 1$).

Normalization:

$$A_N = \left(\frac{m}{2\pi\hbar\varepsilon i}\right)^{\frac{N}{2}} =: \frac{1}{B^N} \tag{5.39}$$

This defines the measure of the path integral, which regularizes the "volume" associated with the infinitesimal spacing ε between the time slices:

$$\boxed{\int \mathcal{D}\{x(\widetilde{t})\} = \lim_{\substack{N\to\infty \\ \varepsilon = t/N}} \frac{1}{B} \int_{-\infty}^{+\infty} \frac{dx_1}{B} \int_{-\infty}^{+\infty} \frac{dx_2}{B} \cdots \int_{-\infty}^{+\infty} \frac{dx_{N-1}}{B}}, \tag{5.40}$$

with

$$B = \sqrt{\frac{2\pi\hbar\varepsilon i}{m}}. \tag{5.41}$$

The summation over all paths yields a path integral. The summation over functions gives, in general, a functional integral.

5.4 Equivalence to the Schrödinger equation

In this section the Schrödinger equation will be derived from the path integral formulation.

Analogies:

Classical	Newton formalism	$\leftrightarrow$	Lagrange formalism
	Local in t		Integral in t
	Differential equation		Least action principle
Quantum mechanical	Schrödinger formalism	$\leftrightarrow$	Feynman formalism

– **Schrödinger formalism:**
Infinitesimal time evolution ($\varepsilon = dt$),

$$|\psi(\varepsilon)\rangle - |\psi(0)\rangle = \frac{-i\varepsilon}{\hbar} H|\psi(0)\rangle + O(\varepsilon^2), \tag{5.42}$$

and in x representation:

$$\begin{aligned} \psi(x,\varepsilon) - \psi(x,0) &= \frac{-i\varepsilon}{\hbar}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x,0) \\ &\quad + O(\varepsilon^2). \end{aligned} \tag{5.43}$$

– **Feynman formalism:**

$$\psi(x,\varepsilon) = \int dx'\, U(x,\varepsilon;x',0)\psi(x',0) \tag{5.44}$$

$$\begin{aligned} U(x,\varepsilon;x',0) &= \int \mathcal{D}\{x(t)\} \exp\Big(+ \frac{i}{\hbar}\int_0^\varepsilon dt' \left[\frac{1}{2}m\dot{x}^2 - V(x)\right]\Big) \\ &= \Big(\frac{m}{2\pi\hbar i\varepsilon}\Big)^{1/2} \int dx' \exp\Big(\frac{i}{\hbar}\Big[\frac{1}{2}m\left(\frac{x-x'}{\varepsilon}\right)^2 - V\left(\frac{x+x'}{2}\right)\Big]\varepsilon\Big) \end{aligned} \tag{5.45}$$

$$O(\varepsilon): \text{ No intermediate time slices} \tag{5.46}$$

$$\begin{aligned} \psi(x,\varepsilon) &= \Big(\frac{m}{2\pi\hbar i\varepsilon}\Big)^{1/2} \int_{-\infty}^{+\infty} dx' \, \exp\Big(i\frac{m}{2\hbar\varepsilon}(x-x')^2\Big) \\ &\quad \times \exp\left(-\frac{i}{\hbar}\varepsilon V\left(\frac{x+x'}{2}\right)\right)\psi(x',0) \end{aligned} \tag{5.47}$$

$$\begin{aligned} &= \Big(\frac{m}{2\pi\hbar i\varepsilon}\Big)^{1/2} \int_{-\infty}^{+\infty} dx' \, \exp\Big(i\frac{m}{2\hbar\varepsilon}y^2\Big) \\ &\quad \times \exp\left(-\frac{i}{\hbar}\varepsilon V\left(\frac{x+x'}{2}\right)\right)\psi(x',0) \end{aligned} \tag{5.48}$$

$$\begin{aligned} &= \Big(\frac{m}{2\pi\hbar i\varepsilon}\Big)^{1/2} \int_{-\infty}^{+\infty} dy \, \exp\Big(i\frac{m}{2\hbar\varepsilon}y^2\Big) \\ &\quad \times \exp\Big(-\frac{i}{\hbar}\varepsilon V(x+y/2)\Big)\psi(x+y,0) \end{aligned} \tag{5.49}$$

In the limit $\varepsilon \to 0$ the factor $\exp\left(i\frac{m}{2\hbar\varepsilon}y^2\right)$ oscillates infinitely rapidly as a function of y so that only the stationary point $y = 0$ contributes to the integral $\int_{-\infty}^{+\infty} dy$. All other factors vary slowly as a function of y.

Expand around $y = 0$ ("infinitesimal propagation"):

$$\psi(x+y,0) = \psi(x,0) + \left.\frac{\partial\psi}{\partial x}\right|_x y + 1/2 \left.\frac{\partial^2\psi}{\partial x^2}\right|_x y^2 + O(y^3) \tag{5.50}$$

$$e^{-\frac{i}{\hbar}\varepsilon V(x+y/2)} = 1 - \frac{i\varepsilon}{\hbar}V(x) + O(\varepsilon y) \tag{5.51}$$

The term $O(\varepsilon y)$ is of higher order than linear in ε and is therefore neglected. Then one obtains:

$$\begin{aligned}\psi(x,\varepsilon) &= \left(\frac{m}{2\pi\hbar i\varepsilon}\right)^{1/2}\int_{-\infty}^{+\infty} dy\, \exp\left(-\frac{m}{2\hbar i\varepsilon}y^2\right)\Big[\psi(x,0) \\ &\quad -\frac{i\varepsilon}{\hbar}V(x)\psi(x,0) + \left.\frac{\partial\psi}{\partial x}\right|_x y + 1/2\left.\frac{\partial^2\psi}{\partial x^2}\right|_x y^2\Big]\end{aligned} \tag{5.52}$$

with

$$\int_{-\infty}^{+\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}} \tag{5.53}$$

$$\int_{-\infty}^{+\infty} dx\, x^2 e^{-ax^2} = -\frac{\partial}{\partial a}\int_{-\infty}^{+\infty} dx\, e^{-ax^2} = \frac{1}{2a}\sqrt{\frac{\pi}{a}} \tag{5.54}$$

it follows

$$\begin{aligned}\psi(x,\varepsilon) &= \left(\frac{m}{2\pi\hbar i\varepsilon}\right)^{1/2}\Big[\left(\frac{2\pi\hbar i\varepsilon}{m}\right)^{1/2}\psi(x,0) + \frac{\hbar i\varepsilon}{2m}\left(\frac{2\pi\hbar i\varepsilon}{m}\right)^{1/2}\frac{\partial^2\psi}{\partial x^2}\Big] \\ &\quad -\left(\frac{m}{2\pi\hbar i\varepsilon}\right)^{1/2}\left[\frac{i\varepsilon}{\hbar}\left(\frac{2\pi\hbar i\varepsilon}{m}\right)^{1/2}V(x)\psi(x,0)\right]\end{aligned} \tag{5.55}$$

$$\psi(x,\varepsilon) - \psi(x,0) = -\frac{i\varepsilon}{\hbar}\Big[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,0) + V(x)\psi(x,0)\Big] \tag{5.56}$$

In the limit $\varepsilon \to 0$ one finally gets

$$\boxed{i\hbar\tfrac{\partial}{\partial t}\psi(x,t)\Big|_{t=0} = \left[-\tfrac{\hbar^2}{2m}\tfrac{\partial^2}{\partial x^2} + V(x)\right]\psi(x,t)\Big|_{t=0}}. \tag{5.57}$$

Thus, the Feynman path integral formulation reproduces the Schrödinger equation. It contains naturally the classical limit for the action $S \gg \hbar$.

5.5 The classical limit

The path integral representation of the propagator U had been constructed such that for macroscopic particles only the classical path $\vec{x}_{\rm cl}(t)$ contributes:

$$U(\vec{x},t;\vec{x}\,',0) = \int_{\vec{x}(0)=\vec{x}\,'}^{\vec{x}(t)=\vec{x}} \mathcal{D}\{\vec{x}(t)\} e^{\frac{i}{\hbar}S\{\vec{x}(t)\}}, \tag{5.58}$$

with the action functional

$$S\{\vec{x}(t)\} = \int_0^t dt' \left(\frac{1}{2}m\dot{\vec{x}}(t')^2 - V(\vec{x}(t'))\right). \tag{5.59}$$

What is the meaning of macroscopic in this context?

Let $V(\vec{x})$ be a potential which varies on a characteristic length scale x_0. If we vary the path $\vec{x} \to \vec{x}(t) + \delta\vec{x}(t)$, and take $|\delta\vec{x}(t)| \ll x_0$ for all times t, then the potential term does not contribute to the variation of the action, and we have

$$\begin{aligned} \delta S\{\vec{x}(t)\} &= \int_0^t dt' \left[m\dot{\vec{x}}(t')\cdot\delta\dot{\vec{x}}(t') - \vec{\nabla}V(\vec{x})\cdot\delta\vec{x}(t')\right] &(5.60)\\ &= -\int_0^t dt' \left[m\ddot{\vec{x}}(t') + \vec{\nabla}V(\vec{x})\right]\cdot\delta\vec{x}(t') + O(\delta x^2), &(5.61)\end{aligned}$$

where in the second step a partial integration was done. The "coherence region" is $\delta S/\hbar < \pi$, i.e. for larger variations, $\delta S/\hbar > \pi$, there is for each path $\vec{x}(t)$ a variation $\vec{x}(t) + \delta\vec{x}(t)$ such that the contributions from the two paths interfere destructively, so that the integral over all those paths vanishes. The condition for this to happen for a given variation $\delta\vec{x}(t)$ is

$$\delta S > \pi\hbar \tag{5.62}$$

or, neglecting the potential term in δS,

$$m > \frac{\pi\hbar}{\left|\int_0^t dt'\,\ddot{\vec{x}}(t)\cot\delta\vec{x}(t)\right|}, \tag{5.63}$$

i.e. for "large enough" mass. There is only one exception to this cancelation of path contributions, namely when for an infinitesimal variation $\delta\vec{x}(t)$ the action does not change at all. This means, that for

$$m > \frac{\pi\hbar}{\left|\int_0^t dt'\,\ddot{\vec{x}}(t)\delta\vec{x}(t)\right|} \tag{5.64}$$

only that path contributes for which $\delta S = 0$. This is the principle of stationary action of classical mechanics, which from above yields the Euler-Lagrange (or Newtonian) equations of motion,

$$m\ddot{\vec{x}} = -\vec{\nabla}V(\vec{x}) = \vec{F}\ . \tag{5.65}$$

Remarks:

1. The condition (5.63) does not set a fixed boundary on the mass m. Rather, it depends on the motion ($\ddot{\vec{x}}$) and on the duration t for which the particle is observed! The larger t, the more quantum effects come into play for a given m. For realistic t, $\ddot{\vec{x}}$ and $m \gtrsim 1g$, quantum effects never play a role. Note that $\ddot{\vec{x}} = 0$ is not possible for *all* variations of the path. After long enough time, any particle becomes quantum mechanical (spread of wave functions), if phase coherence is preserved for all t.

2. Does the condition $\delta S = 0$ with given start and end points of $\vec{x(t)}$ select a unique path?

   The deterministic nature of classical mechanics tells us: in general yes! There are, however, exceptions to this rule in quantum systems which have no classical analogy. These are spin systems, which will be considered later.

The Ehrenfest Theorem

How does the classical motion of a particle emerge from quantum mechanics in detail?

We expect that in the classical limit the quantum mechanical uncertainties in measurements vanish and that each measurement of an observable Ω yields the same value, which must then be equal to the quantum mechanical expectation value. Therefore, we consider the time evolution of the quantum mechanical expectation value:

$$\langle\Omega\rangle = \langle\psi|\Omega|\psi\rangle \tag{5.66}$$

$$\frac{d}{dt}\langle\Omega\rangle = \langle\dot{\psi}|\Omega|\psi\rangle + \langle\psi|\Omega|\dot{\psi}\rangle + \langle\psi|\dot{\Omega}|\psi\rangle \tag{5.67}$$

with

$$|\dot{\psi}\rangle = -\frac{i}{\hbar}H|\psi\rangle \tag{5.68}$$

and

$$\langle\dot{\psi}| = +\frac{i}{\hbar}\langle\psi|H \tag{5.69}$$

it follows

$$\frac{d}{dt}\langle\Omega\rangle = -\frac{i}{\hbar}\langle\psi|(\Omega H - H\Omega)|\psi\rangle + \langle\psi|\dot{\Omega}|\psi\rangle. \tag{5.70}$$

And by that:

$$\boxed{\frac{d}{dt}\langle\Omega\rangle = -\frac{i}{\hbar}\langle[\Omega, H]\rangle + \left\langle\frac{\partial\Omega}{\partial t}\right\rangle} \qquad \text{Ehrenfest theorem} \tag{5.71}$$

The quantum mechanical expectation value evolves in time according to an equation of motion analogous to the classical equation of motion, with

$$\{\Omega, H\} \longrightarrow -\frac{i}{\hbar}[\Omega, H]. \tag{5.72}$$

Reminder:

1. **Expectation value of Ω in state $|\psi\rangle$:**

$$\langle\Omega\rangle = \langle\psi|\Omega|\psi\rangle \tag{5.73}$$

Let $\{|n\rangle\}$ be an eigenbasis of Ω.

$$\begin{aligned}
\Omega|n\rangle &= \omega_n|n\rangle && (5.74)\\
|\psi\rangle &= \sum_n a_n|n\rangle && (5.75)\\
a_n &= \text{contribution of } |n\rangle \text{ to } |\psi\rangle && (5.76)\\
&= \text{amplitude that a particle prepared} \\
&\quad \text{in state } |\psi\rangle \text{ is found in an eigenstate} \\
&\quad |n\rangle \text{ of } \Omega && (5.77)\\
\Rightarrow \langle\psi|\Omega|\psi\rangle &= \sum_n \langle n||a_n|^2\omega_n|n\rangle && (5.78)\\
&= \sum_n |a_n|^2\omega_n && (5.79)\\
&= \text{average value of } \omega_n\text{'s, weighted with the} \\
&\quad \text{probabilities } |a_n|^2 \text{ to find the particle in} \\
&\quad \text{state } |n\rangle. && (5.80)
\end{aligned}$$

2. **Classical motion of a variable Ω:**

$$\Omega = \Omega(\vec{x}, \vec{p}, t) \tag{5.81}$$

With the Hamilton equations of motion,

$$\dot{\vec{x}} = +\frac{\partial H}{\partial \vec{p}}, \quad \dot{\vec{p}} = -\frac{\partial H}{\partial \vec{x}}, \tag{5.82}$$

one gets

$$\begin{aligned} \frac{d}{dt}\Omega &= \frac{\partial \Omega}{\partial \vec{x}}\dot{\vec{x}} + \frac{\partial \Omega}{\partial \vec{p}}\dot{\vec{p}} + \frac{\partial \Omega}{\partial t} && (5.83)\\ &= \frac{\partial \Omega}{\partial \vec{x}}\frac{\partial H}{\partial \vec{p}} - \frac{\partial \Omega}{\partial \vec{p}}\frac{\partial H}{\vec{x}} + \frac{\partial \Omega}{\partial t} && (5.84)\\ &= \{\Omega, H\} + \frac{\partial \Omega}{\partial t}, && (5.85) \end{aligned}$$

where $\{.\,, .\}$ denotes the Poisson brackets.

To obtain a (classical) equation of motion for $\langle\Omega\rangle$, $\frac{d}{dt}\langle\Omega\rangle$ must be related to a function of $\langle\Omega\rangle$ itself, i.e.

$$\frac{d}{dt}\langle\Omega\rangle = \{\langle\Omega\rangle, \langle H\rangle\} + \langle\dot{\Omega}\rangle \; . \tag{5.86}$$

In contrast, the Ehrenfest theorem relates $\frac{d}{dt}\langle\Omega\rangle$ to an expectation value of a function of Ω, $\langle[\Omega, H]\rangle$, which is in general not equivalent. The classical equation of motion for $\langle\Omega\rangle$ will be obtained in the classical limit. To see this, we consider $\Omega = \vec{x}$ and $\Omega = \vec{p}$, since any observable can be constructed from $\vec{x}$, $\vec{p}$.

$$\begin{aligned} \langle\dot{\vec{x}}\rangle &= -\frac{i}{\hbar}\langle[\vec{x}, H]\rangle \quad \text{with} \quad H = \frac{\vec{p}^{\,2}}{2m} + V(\vec{x}) && (5.87)\\ &= -\frac{i}{\hbar}\langle[\vec{x}, \frac{\vec{p}^{\,2}}{2m}]\rangle && (5.88) \end{aligned}$$

With

$$\begin{aligned} [\vec{x}, \vec{p}^{\,2}] &= \vec{p}[\vec{x}, \vec{p}] + [\vec{x}, \vec{p}]\vec{p} && (5.89)\\ &= 2i\hbar\vec{p} && (5.90) \end{aligned}$$

one obtains

$$\langle\dot{\vec{x}}\rangle = \frac{\langle\vec{p}\rangle}{m} = \left\langle\frac{\partial H}{\partial \vec{p}}\right\rangle . \tag{5.91}$$

Analogous, the calculation for $\langle\dot{\vec{p}}\rangle$ yields:

$$\langle\dot{\vec{p}}\rangle = -\frac{i}{\hbar}\langle[\vec{p},H]\rangle = -\frac{i}{\hbar}\langle[\vec{p},V]\rangle \tag{5.92}$$

$$= -\frac{i}{\hbar}\langle(-i\hbar)\frac{\partial V}{\partial\vec{x}}\rangle = -\left\langle\frac{\partial H}{\partial\vec{x}}\right\rangle \tag{5.93}$$

These equations are similar to the Hamilton equations of motion, but to obtain the classical Hamilton equations, we must have

$$\left\langle\frac{\partial H}{\partial\vec{p}}\right\rangle = \frac{\partial\langle H\rangle}{\partial\langle\vec{p}\rangle} \quad \text{and} \quad \left\langle\frac{\partial H}{\partial\vec{x}}\right\rangle = \frac{\partial\langle H\rangle}{\partial\langle\vec{x}\rangle}. \tag{5.94}$$

If H is a quadratic form of $\vec{p}$, $\vec{x}$ only, then these relations hold always.

Proof: Compute $\partial\langle p^2\rangle/\partial\langle p\rangle$

We have

$$\langle(p-\langle p\rangle)^2\rangle = \langle(p^2-2p\langle p\rangle+\langle p\rangle^2\rangle \tag{5.95}$$

$$= \langle p^2\rangle - \langle p\rangle^2 \tag{5.96}$$

$$\Rightarrow \frac{\partial\langle p^2\rangle}{\partial\langle p\rangle} = \frac{\partial\langle(p-\langle p\rangle)^2\rangle}{\partial\langle p\rangle} + \frac{\partial\langle p\rangle^2}{\partial\langle p\rangle} \tag{5.97}$$

$$= \underbrace{2\,\langle(p-\langle p\rangle)(-\underbrace{\frac{\partial\langle p\rangle}{\partial\langle p\rangle}}_{=1})\rangle}_{=0} + 2\langle\vec{p}\rangle \tag{5.98}$$

$$= \left\langle\frac{\partial\vec{p}^{\,2}}{\partial\vec{p}}\right\rangle, \tag{5.99}$$

and analogous

$$\frac{\partial\langle\vec{x}^{\,2}\rangle}{\partial\langle\vec{x}\rangle} = 2\langle\vec{x}\rangle = \left\langle\frac{\partial\vec{x}^{\,2}}{\partial\vec{x}}\right\rangle. \tag{5.100}$$

In general, H is not a quadratic form of $\vec{x}$. In this case, we expand the expectation value of the gradient of the potential appearing in the equation of motion around

the expectation value of $\vec{x}$.

$$\left\langle \frac{\partial H}{\partial \vec{x}} \right\rangle = \langle \vec{\nabla} V(\vec{x}) \rangle =: \langle V'(\vec{x}) \rangle \tag{5.101}$$

$$V'(\vec{x}) = V'(\langle \vec{x} \rangle) + \frac{\partial}{\partial \langle \vec{x} \rangle} V'(\langle \vec{x} \rangle)(\vec{x} - \langle \vec{x} \rangle) \tag{5.102}$$

$$= \frac{\partial}{\partial \langle \vec{x} \rangle} V(\langle \vec{x} \rangle) + \frac{1}{2} \sum_{i,j} \frac{\partial}{\partial \langle x_i \rangle} \frac{\partial}{\partial \langle x_j \rangle} V'(\langle \vec{x} \rangle) (x_i - \langle x_i \rangle)(x_j - \langle x_j \rangle) + \ldots, \tag{5.103}$$

where

$$\vec{x} = (x_1, x_2, x_3)^T. \tag{5.104}$$

Hence we obtain the equations of motion for the expectation values

$$\frac{\partial}{\partial t} \langle \vec{x} \rangle = \frac{\partial \langle H \rangle}{\partial \langle \vec{p} \rangle}, \tag{5.105}$$

which is always valid exactly, since $H \sim \vec{p}^2$, and.

$$\frac{\partial}{\partial t} \langle \vec{p} \rangle = -\left\langle \frac{\partial V}{\partial \vec{x}} \right\rangle \tag{5.106}$$

$$= -\frac{\partial V(\langle \vec{x} \rangle)}{\partial \langle \vec{x} \rangle} - \frac{\partial V(\langle \vec{x} \rangle)}{\partial \langle \vec{x} \rangle} \underbrace{\langle (\vec{x} - \langle \vec{x} \rangle) \rangle}_{=0} - \frac{1}{2} \sum_{i,j} \frac{\partial^2 V'(\langle \vec{x} \rangle)}{\partial \langle \vec{x}_i \rangle \partial \langle \vec{x}_j \rangle} \langle (x_i - \langle x_i \rangle)(x_j - \langle x_j \rangle) \rangle. \tag{5.107}$$

The second derivative appearing in equation (5.107) is the curvature of the classical force.

Discussion of the 2nd equation:

- The first term,

$$-\frac{\partial \langle V(\langle \vec{x} \rangle) \rangle}{\partial \langle \vec{x} \rangle} \equiv -\frac{\partial V(\langle \vec{x} \rangle)}{\partial \langle \vec{x} \rangle}, \tag{5.108}$$

  is just the classical force acting on a particle at position $\langle \vec{x} \rangle$. It reproduces the classical Newton equation of motion.

- The second equals zero, since $\langle(\vec{x} - \langle\vec{x}\rangle)\rangle = 0$.
- The third and higher terms give quantum corrections to the classical limit. They originate from the fact that the wave function is spread out in space:

$$\langle(x_i - \langle\vec{x}_i\rangle)(x_j - \langle\vec{x}_j\rangle)\rangle \neq 0 \tag{5.109}$$

This gives a criterion, when the classical approximation becomes exact:

When the spreading of the wave function is small compared to the scale on which the force $F = -\vec{\nabla}_{\langle\vec{x}\rangle} V(\langle\vec{x}\rangle)$ varies, so that the quantum mechanical position uncertainty becomes irrelevant ($\rightarrow$ WKB approximation).

Chapter 6

Symmetries and Conservation Laws

Definition: Symmetry
A symmetry is a unitary transformation of the Hamilton operator H which leaves H (or the Schrödinger equation) invariant[1].

We then say, the system is symmetric or invariant under a certain transformation.

6.1 Continuous symmetries

Reminder: Classical mechanics
Let $g(\vec{x}, \vec{p})$ be a continuous function of $\vec{x}$, $\vec{p}$. It thus *generates* a canonical transformation of $H(\vec{x}, \vec{p})$:

An infinitesimal canonical transformation, which leaves the equations of motion form invariant, reads:

$$\vec{x} \longrightarrow \vec{x}\,' = \vec{x} + \varepsilon \frac{\partial g}{\partial \vec{p}} =: \vec{x} + \delta\vec{x} \tag{6.1}$$

$$\vec{p} \longrightarrow \vec{p}\,' = \vec{p} - \varepsilon \frac{\partial g}{\partial \vec{x}} =: \vec{p} + \delta\vec{p}, \tag{6.2}$$

[1] In classical mechanics a symmetry is a canonical transformation which leaves the Hamilton function invariant.

with $\varepsilon \to 0$. The Hamiltonian H is then invariant under this infinitesimal transformation.

$$\begin{aligned} 0 &= \delta H = \frac{\partial H}{\partial \vec{x}} \left(\frac{\partial g}{\partial \vec{p}} \cdot \varepsilon \right) - \frac{\partial H}{\partial \vec{p}} \left(\frac{\partial g}{\partial \vec{x}} \cdot \varepsilon \right) && (6.3) \\ &= -\{g, H\}\varepsilon && (6.4) \\ \Rightarrow \frac{dg}{dt} &= \frac{\partial g}{\partial t} = 0 && (6.5) \end{aligned}$$

Since g is not explicitly time dependent, g is therefore conserved.

Quantum mechanical treatment of symmetries

General definitions:

A symmetry must be a unitary transformation acting on the states of Hilbert space and on the Hamiltonian in order to conserve the normalization of a state $|\psi\rangle$.

$$\begin{aligned} |\psi\rangle &\to U|\psi\rangle && (6.6) \\ H &\to UHU^{-1}, \qquad U^\dagger U = 1 && (6.7) \end{aligned}$$

Then U can be written in the form

$$U = e^{-i\alpha G} = \sum_n \frac{1}{n!}(-i\alpha G)^n \,, \tag{6.8}$$

where G is hermitean and $\alpha \in \mathbb{R}$ is a continuous parameter.

The generator G of the transformation

The (infinite) set of transformations U defined in this way forms a group, called Lie group $\mathbb{L}$. This implies an algebra structure for the generators G. The algebra is defined by the commutators $[G_i, G_j]$. If the U's leave the Hamilton operator invariant, $\mathbb{L}$ is called a symmetry group of the Hamiltonian.

Consequences of symmetry groups

Since in quantum mechanics a physical observable G (e.g. $\vec{x}$) does, in general, not have a uniquely defined value, we must formulate the conservation laws in terms of the time independence of the corresponding expectation value $\langle\psi|G|\psi\rangle$

with respect to an *arbitrary* state $|\psi\rangle$.

Theorem: (Quantum analogy of Noether theorem)
If G is a generator of a symmetry group of the Hamiltonian

$$U = e^{-i\alpha G}, \qquad UHU^{-1} = H, \tag{6.9}$$

then G is a conserved quantity, i.e. $\langle\psi|G|\psi\rangle$ is conserved for arbitrary $|\psi\rangle$.

Proof: Let α be infinitesimal so that we can expand U as

$$U = 1 - i\alpha G + O(\alpha^2). \tag{6.10}$$

Since H is invariant under the transformation U (6.9), we yield

$$\begin{aligned} H &= (1 - i\alpha G)H(1 + i\alpha G) && (6.11)\\ &= H - i\alpha GH + i\alpha HG && (6.12)\\ &= H - i\alpha[G, H] && (6.13)\\ \Leftrightarrow\ [G, H] &= 0 && (6.14) \end{aligned}$$

And by that we finally get

$$\frac{d}{dt}\langle\psi|G|\psi\rangle = -\frac{i}{\hbar}\langle\psi|[G, H]|\psi\rangle = 0, \quad \forall\,|\psi\rangle, \tag{6.15}$$

where the Ehrenfest theorem was used.

Lemma:
One can find a simultaneous eigenbasis of the Hamiltonian H and of the generator G of a symmetry of H, since $[G, H] = 0$.

The symmetry analysis is useful, since eigenstates of G are often easier to find than those of H[2].

[2]**Reminder:** For commuting operators, $[G, H] = 0$, there exists a simultaneous eigenbasis, where G and H are hermitean operators.

Proof:
Let $|\psi\rangle$ be an arbitrary eigenvector of G with eigenvalue λ, i.e.

$$G|\psi\rangle = \lambda|\psi\rangle. \tag{6.16}$$

One then obtains

$$GH|\psi\rangle = HG|\psi\rangle = \lambda H|\psi\rangle, \tag{6.17}$$

which means that $|\widetilde{\psi}\rangle \equiv H|\psi\rangle$ is eigenvector of G with the same eigenvalue λ.

1. If λ is non-degenerate, i.e. 2 linearly independent eigenvectors of G with the same eigenvalue λ do not exist, then

   $$|\widetilde{\psi}\rangle = E|\psi\rangle \ , \quad E \in \mathbb{C}. \tag{6.18}$$

   where $|\widetilde{\psi}\rangle$ is proportional to $|\psi\rangle$. Furthermore $|\psi\rangle$ eigenvector of H, because

   $$H|\psi\rangle \equiv |\widetilde{\psi}\rangle = E|\psi\rangle. \tag{6.19}$$

2. If λ is m-fold degenerate, then

   - there exists a subspace V_λ with basis $\{|\psi_1\rangle, \ldots, |\psi_m\rangle\}$ of eigenstates of G with eigenvalues λ.
   - V_λ is closed with respect to H, i.e.

     $$|\psi\rangle \in V_\lambda \quad \Rightarrow \quad H|\psi\rangle = |\widetilde{\psi}\rangle \in V_\lambda. \tag{6.20}$$

   Find an eigenbasis of H in the eigenvector space V_λ of G.

The question now is how to obtain the conserved generator of a symmetry. Some important examples are given in the following subsections.

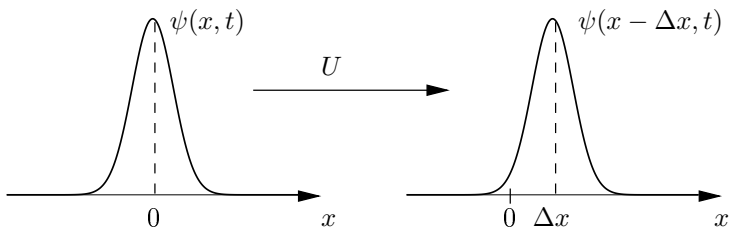

Figure 6.1: Propagation of a wave packet

6.1.1 Translation invariance in position space

- For simplicity we first consider the case $d = 1$:

$$\begin{aligned} U\psi(x,t) &= \psi(x-\Delta x,t) \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \left.\frac{\partial^n \psi}{\partial x^n}\right|_x \Delta x^n \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\Delta x \frac{\partial}{\partial x}\right)^n \psi(x) \\ &= \exp\left(-i\Delta x \left(-i\frac{\partial}{\partial x}\right)\right) \psi(x,t) \\ U_x &\equiv e^{-i\Delta x G_x}, \end{aligned}$$

  which is equivalent to

$$\boxed{G_x = -i\tfrac{\partial}{\partial x} = \tfrac{p_x}{\hbar}}. \tag{6.21}$$

  Therefore the momentum operator is the generator of the translation group.

- Now consider the case $d = 3$:

$$G_{x_j} = \frac{p_j}{\hbar}, \quad j = x,\, y,\, z \tag{6.22}$$

$$[p_j, p_k] = 0 \qquad \text{(commutative group)} \tag{6.23}$$

  The general translation operator then reads

$$U = U_x U_y U_z \,(= U_y U_x U_z \text{ etc.}) \tag{6.24}$$

$$= e^{-i\Delta x \frac{P_x}{\hbar}} e^{-i\Delta y \frac{p_y}{\hbar}} e^{-i\Delta z \frac{p_z}{\hbar}} \tag{6.25}$$

$$= e^{-i\Delta \vec{x} \frac{\vec{p}}{\hbar}} \tag{6.26}$$

It follows from the quantum Noether theorem that in a translationally invariant system the momentum is conserved, i.e. the momentum expectation value $\langle \vec{p} \rangle$ is conserved for any state evolving according to the (time-dependent) Schrödinger equation.

6.1.2 Time translation invariance

$$U\psi(x,t) = \psi(x, t - \Delta t) \tag{6.27}$$

The generator of the temporal translation is, in analogy,

$$G_t = -i\frac{\partial}{\partial t} = -\frac{\widehat{E}}{\hbar}. \tag{6.28}$$

if H is not explicitly time dependent, the energy is conserved.

6.1.3 Internal continuous symmetries: gauge invariance

These symmetries have no analogon in classical physics! We consider first a global (x, t independent) phase transformation of a wave function, a $U(1)$ gauge transformation,

$$U\psi(\vec{x},t) = e^{-i\phi}\psi(\vec{x},t) = \psi'(\vec{x},t). \tag{6.29}$$

The Hamiltonian is invariant, since $\phi(\vec{x}) = \text{const.}$,

$$e^{-i\phi}He^{i\phi} = H. \tag{6.30}$$

The generator of the phase transformation is in this representation obviously $G_\phi = 1$. Hence we have the conserved quantity

$$0 = \frac{d}{dt}\langle\psi|1|\psi\rangle = \frac{d}{dt}\int d^3x\, \psi^*(\vec{x},t)\psi(\vec{x},t) = \frac{d}{dt}N\ . \tag{6.31}$$

The global $U(1)$ gauge symmetry implies that the total particle number, i.e. the integral of the probability density, is conserved.

Local $U(1)$ gauge symmetry

We postulate that the Schrödinger equation shall be form invariant under $U(1)$ gauge transformations (Yang-Mills).

$$\begin{aligned}
\psi'(\vec{x},t) &= e^{+i\theta(\vec{x},t)}\psi(\vec{x},t) && (6.32)\\
i\hbar\frac{\partial}{\partial t}\psi &\stackrel{!}{=} -\frac{\hbar^2}{2m}\vec{\nabla}^{\,2}\psi + V(x)\psi && (6.33)\\
i\hbar\frac{\partial'}{\partial t}\psi' &= -\frac{\hbar^2}{2m}\vec{\nabla}'^{\,2}\psi' + V(x)\psi' && (6.34)\\
\vec{\nabla}\psi'(\vec{x},t) &= \vec{\nabla}e^{+i\theta(\vec{x},t)}\psi(\vec{x},t) && (6.35)\\
&= e^{+i\theta(\vec{x},t)}[\vec{\nabla}\psi(\vec{x},t)] + i[\vec{\nabla}\theta(\vec{x},t)]\underbrace{e^{+i\theta(\vec{x},t)}\psi(\vec{x},t)}_{=\psi'(\vec{x},t)} && (6.36)
\end{aligned}$$

The $\vec{\nabla}\theta$ term breaks the form invariance of the derivative. Therefore we have to define a *covariant derivative*, which compensates the $\vec{\nabla}\theta$ term.

$$\begin{aligned}
\vec{\nabla} &\longrightarrow \vec{\nabla}\,' = \vec{\nabla} - i\frac{\partial\theta(\vec{x},t)}{\partial\vec{x}} \quad \text{(covariant derivative)} && (6.37)\\
\vec{p} = -i\hbar\vec{\nabla} &\longrightarrow \vec{p}\,' = \vec{p} - \hbar\frac{\partial\theta}{\partial\vec{x}} \quad \text{(kinetic momentum)}, && (6.38)
\end{aligned}$$

and similarly

$$\begin{aligned}
\frac{\partial}{\partial t} &\longrightarrow \frac{\partial\,'}{\partial t} = \frac{\partial}{\partial t} - i\frac{\partial\theta(\vec{x},t)}{\partial t} \quad \text{(covariant derivative)} && (6.39)\\
E = i\hbar\frac{\partial}{\partial t} &\longrightarrow i\hbar\frac{\partial\,'}{\partial t} = i\hbar\frac{\partial}{\partial t} + \hbar\frac{\partial\theta}{\partial t}. && (6.40)
\end{aligned}$$

In the presence of local gauge invariance, the Schrödinger equation must be generalized to

$$\left[i\hbar\frac{\partial}{\partial t} + \hbar\frac{\partial\theta}{\partial t}\right]\psi(\vec{x},t) = \left[\frac{1}{2m}\left(\vec{p} - \hbar\frac{\partial\theta}{\partial\vec{x}}\right)^2 + V(\vec{x})\right]\psi(\vec{x},t), \tag{6.41}$$

i.e., *gradient fields* must be added to the derivatives, which does not change the physics. The generalization to general fields yields

$$\begin{aligned}
\frac{e}{c}\vec{A} &= \hbar\frac{\partial\theta}{\partial\vec{x}} \quad \Leftrightarrow \quad \frac{\partial\theta}{\partial\vec{x}} = \frac{e}{\hbar c}\vec{A} && (6.42)\\
e\vec{\phi} &= -\hbar\frac{\partial\theta}{\partial t} \quad \Leftrightarrow \quad -\frac{1}{c}\frac{\partial\theta}{\partial t} = \frac{e}{\hbar c}\phi. && (6.43)
\end{aligned}$$

The electromagnetic 4-vector potential reads

$$\partial_\mu \theta \longrightarrow \frac{e}{\hbar c} a^\mu = \frac{e}{\hbar c} \begin{pmatrix} \phi \\ \vec{A} \end{pmatrix} \tag{6.44}$$

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{x}, t) = \Big[\frac{1}{2m} \Big(\vec{p} - \frac{e}{c} \vec{A} \Big)^2 + e\phi(\vec{x}, t) + V(\vec{x}) \Big] \psi(\vec{x}, t). \tag{6.45}$$

6.2 Discrete Symmetries

6.2.1 Parity: Space inversion symmetry

The action of the parity operator P is defined by

$$P: \quad \vec{x} \longrightarrow -\vec{x}, \tag{6.46}$$

where $\vec{x}$ is a position vector. Now we want to derive the eigenvalues of P.

First of all, the definition of P yields

$$P^2 = 1. \tag{6.47}$$

If $|\psi\rangle$ is an eigenstate of P, we get

$$P|\psi\rangle = \lambda_P |\psi\rangle \tag{6.48}$$

$$P^2|\psi\rangle = \lambda_P^2 |\psi\rangle \tag{6.49}$$

$$\Leftrightarrow |\psi\rangle = \lambda_P^2 |\psi\rangle, \tag{6.50}$$

and therefore

$$\lambda_P^2 = 1. \tag{6.51}$$

Thus the eigenvalues of P are

$$\boxed{\lambda_P = \begin{cases} +1 & , \text{ even parity} \\ -1 & , \text{ odd parity} \end{cases}}. \tag{6.52}$$

If the Hamiltonian, i.e. the potential, is invariant under space inversion (parity symmetries), then the eigenfunctions of H in position representation must be

either symmetric ($\lambda_P = +1$) or antisymmetric ($\lambda_P = -1$) with respect to space inversion.

We have encountered this property before in problems of a particle in a one-dimensional, symmetric potential well and the harmonic oscillator.

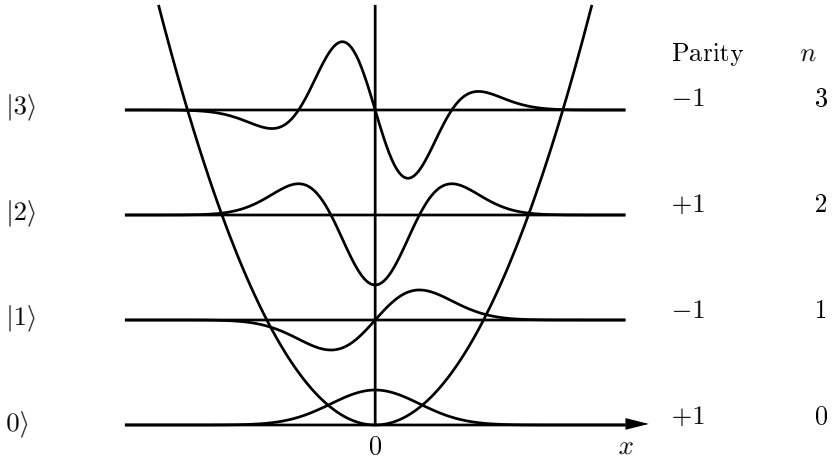

Figure 6.2: Alternating parity, $\lambda_p = (-1)^n$, of the harmonic oscillator eigenfunctions

Proof:
The ground state $|0\rangle$ has even parity $\lambda_P = +1$. An arbitrary state $|n\rangle$ can be generated by letting act $a^\dagger$ n-times on $|0\rangle$, i.e.

$$|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n|0\rangle. \tag{6.53}$$

Expressing the creation operator through the position and momentum operators, we get in position representation for the state $|n\rangle$

$$\psi_n(x) = \frac{1}{\sqrt{n!}}\Bigg(\underbrace{\sqrt{\frac{m\omega}{2\hbar}}x - i\sqrt{\frac{1}{2m\hbar\omega}}\left(-i\hbar\frac{\partial}{\partial x}\right)}_{a^\dagger}\Bigg)^n \psi_0(x). \tag{6.54}$$

The action of P onto the creation operator gives

$$Pa^\dagger = -a^\dagger, \tag{6.55}$$

and the parity of $|n\rangle$ is therefore given by $(-1)^n$.

In the following we summarize the parity transformation of the operators $\widehat{\vec{x}}, \widehat{\vec{p}}$ and $\widehat{\vec{E}}$.

$$\widehat{\vec{x}} \longrightarrow -\widehat{\vec{x}} \tag{6.56}$$

$$\widehat{\vec{p}} \longrightarrow -\widehat{\vec{p}}, \qquad \text{since} \qquad \widehat{\vec{p}} = -i\hbar\frac{\partial}{\partial \vec{x}} \tag{6.57}$$

$$\widehat{E} \longrightarrow \widehat{E}, \qquad \text{since} \qquad \widehat{E} = i\hbar\frac{\partial}{\partial t} \tag{6.58}$$

6.2.2 Time reversal symmetry

The action of the time reversal operator T is given by

$$t \longrightarrow -t \tag{6.59}$$

$$\vec{x} \longrightarrow \vec{x} \tag{6.60}$$

$$\vec{p} \longrightarrow -\vec{p}, \tag{6.61}$$

where t is the time coordinate. The transformation of wave functions under time reversal in a time reversal symmetric system is given by

$$THT^{-1} = H \tag{6.62}$$

$$i\hbar\frac{\partial}{\partial t}\psi = H\psi, \tag{6.63}$$

and

$$T\left(i\hbar\frac{\partial}{\partial t}\psi\right) = TH\psi \tag{6.64}$$

$$\Leftrightarrow\ -i\hbar\frac{\partial}{\partial t}T\psi = HT\psi, \tag{6.65}$$

which is equivalent to

$$\boxed{\begin{array}{lccc} T: & \psi & \longrightarrow & \psi^* \\ & \left(-i\hbar\frac{\partial}{\partial \vec{x}}\right) & \longrightarrow & \left(-i\hbar\frac{\partial}{\partial \vec{x}}\right)^* \end{array}}. \tag{6.66}$$

The time reversal symmetry is broken in an *external* magnetic field, which is not time reversed.

Chapter 7

Angular momentum and rotational invariance

Rotationally invariant problems are of great importance in physics. This class of problems includes all systems with a central-symmetric potential, for instance the Coulomb potential, i.e. atomic systems etc. Although being highly symmetric and, hence, having a large number of conserved quantities, these systems are sufficiently complex to have interesting dynamics.
In this chapter we consider rotational invariance and the conservation laws that follow from it.

7.1 Lie Algebra, Lie group, basics of representation theory

In contrast to translations, rotations about different axes in 3-dimensional space and, hence, their generators do not commute with each other.
Moreover, later on we will need to perform rotations of different objects, (scalar) wave functions, vectors in 3-dimensional position space, and so-called spinors. This means, we will need to represent the general rotation group as linear rotation operators acting in different vector spaces, e.g. the space of square-integrable functions S, 3-dimensional vector space etc. Therefore it is useful to consider continuous groups, like the rotation group, and the algebra of their generators on a

more general level. Motivated by the central importance of the commutator of two operators, we define:

Definition: Lie algebra A

1. A is a real vector space
2. Within A there exists a bilinear, scew-symmetric mapping $[\cdot,\cdot]$, called "Lie product", which the properties

$$\begin{aligned} A \times A &\rightarrow A & (7.1)\\ (a,b) &\mapsto c \qquad a,b,c \in A & (7.2) \end{aligned}$$

   with

$$[a,b] = -[b,a]. \tag{7.3}$$

3. This Lie product fulfills the Jacobi identity:

$$[a,[b,c]] + [b,[c,a]] + [c,[a,b]] = 0, \quad \forall a,b,c \in A \tag{7.4}$$

One may identify the vector space of linear operators on Hilbert space with A and the Lie product with the commutator $[a,b] = ab - ba$. This identification obeys the conditions 1.-3.

Definition: Lie group $\mathcal{G}$
Is A the Lie algebra spanned by a set of hermitean operators

$$\{G_n | G_n^\dagger = G_n, n = 1,\ldots,N\}, \tag{7.5}$$

the generators of $\mathcal{G}$, then the group of unitary transformations

$$U_n(\alpha) = e^{-i\alpha G_n}, \qquad \alpha \in \mathbb{R} \tag{7.6}$$

is called the Lie group belonging to A. Using the above definitions, the commutator $[G_n, G_m]$ of two operators of the Lie algebra specifies the structure of the group $\mathcal{G}$ in a general way by prescribing how consecutive group transformations $U_n(\alpha)$ have to be applied. In order to perform such a transformation acting on a concrete vector space V (e.g. function space S, position space) the elements

of the group, or of the generators of $\mathcal{G}$, must be represented as operators in a concrete way. This leads to the definition of a representation.

Definition: Representation D of an algebra A
Let V be a complex vector space and let $L(V)$ be the vector space of linear transformations on V. The mapping $D: A \longrightarrow L(V)$ is called representation of the algebra A in the vector space V, if D is compatible with $[\cdot,\cdot]$, i.e. if

$$[D(a), D(b)] = D([a,b]) \quad \forall a, b \in A \tag{7.7}$$

yields with

$$[D(a), D(b)] := D(a)D(b) - D(b)D(a). \tag{7.8}$$

This requirement ensures that the algebra structure is preserved by the representation.

Abstract algebra	a,	b,	c	$[a,b]$	$=$	c
	$\downarrow$	$\downarrow$	$\downarrow$			
Linear transformations	$D(a)$	$D(b)$	$D(c)$	$D([a,b])$	$=$	$D(c)$

Definition: Irreducible representation
The representation D in a d-dimensional vector space V is irreducible, if there is *no* vector subspace $V' \subset V$with dimension $d' < d$, such that V' is invariant under D,

$$D(a)v = w \ \in V' \qquad \forall v \in V',\, a \in A\,. \tag{7.9}$$

This can be visualized in terms of matrices:

- **Vectors $v \in V$ in coordinate representation:**

$$v = \begin{pmatrix} v_1 \\ \vdots \\ v_d \end{pmatrix} \tag{7.10}$$

- **Transformations $D(a)$ on V are matrices:**

$$D(a) = \begin{pmatrix} D_1 & & & 0 \\ & D_2 & & \\ & & D_3 & \\ 0 & & & D_4 \end{pmatrix} \tag{7.11}$$

$$D(a) = (D_1) \tag{7.12}$$

Equation (7.11) describes a reducible representation and equation (7.12) an irreducible representation.

The above definitions will be filled with meaning by the example of the angular momentum algebra.

7.2 Angular momentum algebra: generators of the rotation group and angular momentum conservation

We expect that the conserved quantity connected with rotational invariance is the angular momentum, like in classical mechanics and in analogy to the connection between translational invariance and linear momentum.
In the following we will first define and analyze the angular momentum operator and then construct explicitly the generators of the rotation group for rotations of scalar wave functions $\psi(\vec{r})$.

Angular momentum in quantum mechanics
We choose the x-representation and let $\widehat{\vec{L}}$ act on wave functions $\psi(\vec{x},t)$. In classical mechanics the angular momentum is given by

$$L = [\vec{x} \times \vec{p}]. \tag{7.13}$$

The correspondence principle gives us the quantum mechanical operator which reads

$$\boxed{\widehat{\vec{L}} = \widehat{\vec{x}} \times \widehat{\vec{p}} = \vec{x} \times (-i\hbar\vec{\nabla})}. \tag{7.14}$$

In the following the $\widehat{\ }$ is only used for operators if confusion with classical quantities may arise.

$$\left.\begin{aligned} L_x &= -i\hbar\left(y\tfrac{\partial}{\partial z} - z\tfrac{\partial}{\partial y}\right) \\ L_y &= -i\hbar\left(z\tfrac{\partial}{\partial y} - y\tfrac{\partial}{\partial z}\right) \\ L_z &= -i\hbar\left(x\tfrac{\partial}{\partial y} - y\tfrac{\partial}{\partial x}\right) \end{aligned}\right\} \boxed{L_k = -i\hbar\varepsilon_{klm}x_l\tfrac{\partial}{\partial x_m}} \tag{7.15}$$

Note here the sum convention, i.e. doubly appearing indices are summed over.

Complications of the quantum mechanical description

1. The quantum mechanical definition of $\vec{L}$ is not unique, since

$$[\widehat{\vec{r}} \times \widehat{\vec{p}}] \neq -[\widehat{\vec{p}} \times \widehat{\vec{r}}], \tag{7.16}$$

where the minus sign is the trivial sign of the classical expression. As will become obvious below,

$$\widehat{\vec{L}} = [\widehat{\vec{r}} \times \widehat{\vec{p}}] \tag{7.17}$$

is the physically correct choice of the definition for $\widehat{\vec{L}}$ being the generators of rotations.

2. Rotations in $d = 3$ dimensions do not commute in general, in contrast to linear translations. $R_{\widehat{\alpha}}(\varphi)$ represents a rotation around the axis $\widehat{\alpha}$ by the angle φ.

Example:

$$R_{\widehat{x}}\left(\frac{\pi}{2}\right) R_{\widehat{z}}\left(\frac{\pi}{2}\right) \widehat{e}_x = R_{\widehat{x}}\left(\frac{\pi}{2}\right) \widehat{e}_y = \widehat{e}_z, \tag{7.18}$$

but

$$R_{\widehat{z}}\left(\frac{\pi}{2}\right) R_{\widehat{x}}\left(\frac{\pi}{2}\right) \widehat{e}_x = R_{\widehat{z}}\left(\frac{\pi}{2}\right) \widehat{e}_x = \widehat{e}_y. \tag{7.19}$$

It will be shown below that the angular momentum operators L_x, L_y, L_z are the generators of the rotation group in three dimensions. Correspondingly, the components L_x, L_y, L_z of $\vec{L}$ do not commute. Using the definition $L_k = \varepsilon_{klm} x_l p_m$ and $[x_l, p_m] = i\hbar\delta_{lm}$ the non-commutation can be shown explicitly.

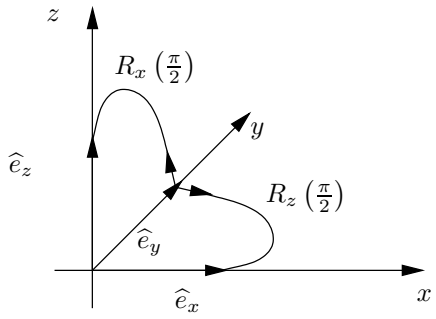

Figure 7.1: Example of non-commutation of rotations

Proof of commutation relation

$$
\begin{aligned}
[L_k, L_l] &= \varepsilon_{kmn}\varepsilon_{lm'n'}[x_m p_n, x_{m'} p_{n'}] && (7.20)\\
&= \varepsilon_{kmn}\varepsilon_{lm'n'}\{x_m[p_n, x_{m'}]p_{n'} + x_{m'}[x_m, p_{n'}]p_n\} && (7.21)\\
&= \varepsilon_{kmn}\varepsilon_{lm'n'}\{-x_m i\hbar\delta_{nm'}p_{n'} + x_{m'} i\hbar\delta_{mn'}p_n\} && (7.22)\\
&= i\hbar\varepsilon_{kmn}\{-\varepsilon_{lnn'}x_m p_{n'} + \varepsilon_{lm'm}x_{m'}p_n\} && (7.23)\\
&= i\hbar\varepsilon_{kmn}\varepsilon_{ln'n}x_m p_{n'} - i\hbar\varepsilon_{knm}\varepsilon_{lm'm}x_{m'}p_n && (7.24)\\
&= i\hbar\left(\delta_{kl}\delta_{mn'} - \delta_{kn'}\delta_{ml}\right)x_m p_{n'}\\
&\quad -i\hbar\left(\delta_{kl}\delta_{nm'} - \delta_{km'}\delta_{nl}\right)x_{m'}p_n && (7.25)\\
&= i\hbar\Big\{\delta_{kl}\sum_m x_m p_m - x_l p_k - \delta_{kl}\sum_n x_n p_n + x_k p_l\Big\} && (7.26)\\
&= i\hbar(x_k p_l - x_l p_k) && (7.27)\\
&= i\hbar\varepsilon_{klm}L_m && (7.28)
\end{aligned}
$$

In the following we summarize these really important relations.

$$
\boxed{
\begin{aligned}
[L_k, L_m] &= i\hbar\varepsilon_{klm}L_m\\
[L_x, L_y] &= i\hbar L_z\\
[L_y, L_z] &= i\hbar L_x\\
[L_z, L_x] &= i\hbar L_y
\end{aligned}
} \qquad (7.29)
$$

The non-trivial commutation rules of L_x, L_y, L_z imply

- that not all 3 components of $\vec{L}$ can simultaneously be measured with arbitrary precision (uncertainty principle) and
- that the eigenstates of a rotationally invariant system are uniquely characterized by less than 3 components of $\vec{L}$!

The profound consequences of this uncertainty will be analyzed in section 7.4.

Representation in spherical coordinates
(=choice of basis of $\vec{x}$-space)

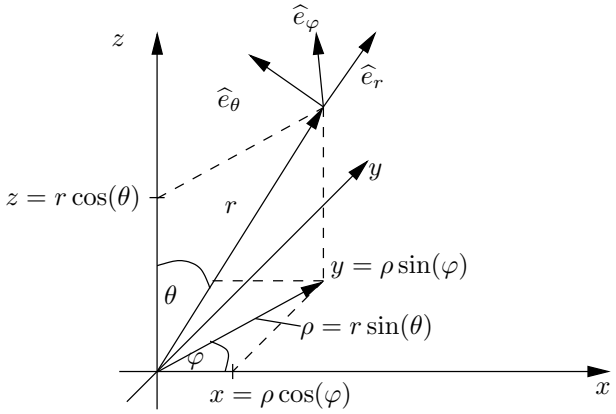

Figure 7.2: Spherical coordinates

The vectors $\widehat{e}_r, \widehat{e}_\varphi$ and $\widehat{e}_\theta$ form a local orthonormal coordinate system which is dependent of the considered point. The components of the cartesian vector $\vec{x}$ read in spherical coordinates,

$$x = r\cos(\varphi)\sin(\theta) \tag{7.30}$$
$$y = r\sin(\varphi)\sin(\theta) \tag{7.31}$$
$$z = r\cos(\theta). \tag{7.32}$$

Now we want to express the components of the angular momentum operator $\vec{L}$ in spherical coordinates. In order to do this we first have to express the gradient in spherical coordinates, because $\vec{L}$ contains the momentum operator $\vec{p} = -i\hbar\vec{\nabla}$.

In cartesian coordinates the gradient reads

$$\vec{\nabla} = \widehat{e}_x \frac{\partial}{\partial x} + \widehat{e}_y \frac{\partial}{\partial y} + \widehat{e}_z \frac{\partial}{\partial z} = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix}. \tag{7.33}$$

To express this in spherical coordinates we have to derive the directional derivatives along the axes of the local orthonormal coordinate system $\widehat{e}_r, \widehat{e}_\varphi, \widehat{e}_\theta$.

$$\vec{\nabla} = \widehat{e}_r \frac{\partial}{\partial r} + \widehat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \widehat{e}_\varphi \frac{1}{r \sin(\theta)} \frac{\partial}{\partial \varphi} = \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{1}{r} \frac{\partial}{\partial \theta} \\ \frac{1}{r \sin(\theta)} \frac{\partial}{\partial \varphi} \end{pmatrix} \tag{7.34}$$

The basis transformation from the cartesian to the spherical system is done by

$$\frac{\partial}{\partial r} = \sum_{x_i = x,y,z} \frac{\partial x_i}{\partial r} \frac{\partial}{\partial x_i} \tag{7.35}$$

$$\frac{1}{r} \frac{\partial}{\partial \theta} = \frac{1}{r} \sum_{x_i = x,y,z} \frac{\partial x_i}{\partial \theta} \frac{\partial}{\partial x_i} \tag{7.36}$$

$$\frac{1}{r \sin(\theta)} \frac{\partial}{\partial \varphi} = \frac{1}{r \sin(\theta)} \sum_{x_i = x,y,z} \frac{\partial x_i}{\partial \varphi} \frac{\partial}{\partial x_i}. \tag{7.37}$$

One therefore obtains

$$\begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{1}{r} \frac{\partial}{\partial \theta} \\ \frac{1}{r \sin(\theta)} \frac{\partial}{\partial \varphi} \end{pmatrix} = \underbrace{\begin{pmatrix} \cos(\varphi)\sin(\theta) & \sin(\varphi)\sin(\theta) & \cos(\theta) \\ \cos(\varphi)\cos(\theta) & \sin(\varphi)\cos(\theta) & -\sin(\theta) \\ -\sin(\varphi) & \cos(\varphi) & 0 \end{pmatrix}}_{U(r,\theta,\varphi)} \times \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} \tag{7.38}$$

$$\begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} = U^T \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{1}{r} \frac{\partial}{\partial \theta} \\ \frac{1}{r \sin(\theta)} \frac{\partial}{\partial \varphi} \end{pmatrix}, \tag{7.39}$$

where $U(r, \theta, \varphi)$ is an orthonormal transformation. The cartesian components of $\vec{L}$ expressed in spherical coordinates using the orthonormal transformation

$U^{-1}(r,\theta,\varphi)$ read

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = -i\hbar \begin{pmatrix} 0 & -z & y \\ z & 0 & -x \\ -y & x & 0 \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} \tag{7.40}$$

$$= -i\hbar \begin{pmatrix} 0 & -z & y \\ z & 0 & -x \\ -y & x & 0 \end{pmatrix} U^T \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{1}{r}\frac{\partial}{\partial \theta} \\ \frac{1}{r\sin(\theta)}\frac{\partial}{\partial \varphi} \end{pmatrix}. \tag{7.41}$$

Multiplying this products out an plugging in the spherical coordinates for x, y, z one finally gets

$$\boxed{\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} i\hbar\left(\sin(\varphi)\frac{\partial}{\partial\theta} + \cos(\varphi)\cot\theta\frac{\partial}{\partial\varphi}\right) \\ i\hbar\left(-\cos(\varphi)\frac{\partial}{\partial\theta} + \sin(\varphi)\cot\theta\frac{\partial}{\partial\varphi}\right) \\ -i\hbar\frac{\partial}{\partial\varphi} \end{pmatrix}}. \tag{7.42}$$

Generator of rotations about an arbitrary axis $\widehat{a}$: $R_{\widehat{a}}(\Delta\varphi)$
Representation in function space S:

$$D_S(R_{\widehat{a}}(\Delta\varphi))\psi(\vec{x}) = \psi(D_x(R_{\widehat{a}}^{-1}(\Delta\varphi))\vec{x}) \tag{7.43}$$

Often, the shorthand notation $D(R) \to R$ is used, identifying the representation with the transformation itself,

$$R_{\widehat{a}}(\Delta\varphi)\psi(\vec{x}) = \psi(R_{\widehat{a}}^{-1}(\Delta\varphi)\vec{x}). \tag{7.44}$$

Without loss of generality we choose $\widehat{e}_z || \vec{a}$ and then obtain

$$R_{\widehat{a}\equiv z}(\Delta\varphi)\psi(r,\theta,\varphi) = \psi(r,\theta,\varphi-\Delta\varphi) \tag{7.45}$$

$$= \sum_{n=0}^{\infty} \frac{1}{n!}\frac{\partial^n\psi}{\partial\varphi^n}\bigg|_{(r,\theta,\varphi)} (-\Delta\varphi)^n \tag{7.46}$$

$$= e^{-\Delta\varphi\frac{\partial}{\partial\varphi}}\psi(r,\theta,\varphi) \tag{7.47}$$

$$= e^{-i\Delta\varphi\frac{L_z}{\hbar}}\psi(r,\theta,\varphi). \tag{7.48}$$

Therefore $\frac{1}{\hbar}\vec{L} = \frac{[\vec{x}\times\vec{p}]}{\hbar}$ are the generators of the rotation group and the commutator $[L_i, L_j] = i\hbar\varepsilon_{ijk}L_k$ is the angular momentum algebra. In a rotationally invariant system, $[L_i, H] = 0$, the angular momentum L_i is conserved, i.e.

$$\frac{d}{dt}\langle\psi|L_i|\psi\rangle = 0, \quad \forall|\psi\rangle \quad \text{with} \quad i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle. \tag{7.49}$$

Furthermore $U_{\vec{a}} = e^{-i\vec{a}\vec{L}/\hbar}$ describes a rotation about axis $\vec{a}$ by the angle $|\vec{a}|$.

7.3 Eigenstates of L_z: 2-dimensional rotations

The z-component of $\vec{L}$ is given by

$$L_z = -i\hbar\frac{\partial}{\partial\varphi}. \tag{7.50}$$

The eigenstates of L_z, in $\vec{x}$-representation, are analogous to the p eigenstates and read

$$\psi_m(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi} \tag{7.51}$$

with the eigenvalue $m\hbar$ and r, θ arbitrary. The prefactor in (7.51) arises due to normalization. But the wave function must have a unique value by rotations by an angle of 2π, i.e.

$$\psi_m(\varphi - 2\pi) = \psi_m(\varphi). \tag{7.52}$$

This condition together with (7.51) immediately gives us

$$\boxed{m \in \mathbb{Z} \text{ integer}}, \tag{7.53}$$

where m is from now on called the magnetic angular momentum quantum number. From this we see that again, boundary condition induces quantization.

7.4 The eigenvalue problem of $\vec{L}$ in 3 dimensions

Consider a rotationally invariant system,

$$[L_i, H] = 0, \quad i = x, y, z. \tag{7.54}$$

Although all 3 components of $\vec{L}$ commute with H, they do not commute with each other. This means that there are no simultaneous eigenstates of L_x, L_y, L_z. The eigenstates of angular momentum must be uniquely characterized by less than 3 (conserved) quantum numbers.
In order to characterize the eigenstates of a rotationally invariant system completely, we must find a maximal set of operators which

- are built out of L_x, L_y, L_z and, thus, commute with H,

- all commute among each other.

Obviously, the number of such operators is less than 3.

We can choose[1] the modulus squared of $\vec{L}$ (or length),

$$\vec{L}^{\,2} = L_x^2 + L_y^2 + L_z^2, \tag{7.55}$$

and the z-component L_z since

$$[\vec{L}^{\,2}, L_i] = 0 \quad , i = x, y, z. \tag{7.56}$$

Remarks:

- Once the "length" of $\vec{L}$ is fixed, i.e. $\vec{L}^{\,2}$, only one component of $\vec{L}$ can be determined sharply in any given state.
- An operator which commutes with all operators of an algebra A and, hence, with the whole group $\mathcal{G}$, is called *Casimir operator*.

  Example: $\vec{L}^{\,2}$ for angular momentum algebra

7.4.1 Eigenstates and eigenvalues of $\vec{L}^{\,2}$ and L_z

The eigenstates and eigenvalues of $\vec{L}^{\,2}$and L_z could be determined in position representation by solving the differential equations corresponding to the eigenvalue equations with the boundary condition of uniqueness of the wave function, analogous to the case $d = 2$ in section 7.3.
Instead we follow here the algebraic solution method, analogous to the harmonic oscillator problem, since it will provide further insight into the structure of the angular momentum algebra.

Let $|\alpha\beta\rangle$ be simultaneous eigenstates of $\vec{L}^{\,2}$ and L_z, i.e.

$$\vec{L}^{\,2}|\alpha\beta\rangle = \alpha|\alpha\beta\rangle \tag{7.57}$$

$$L_z|\alpha\beta\rangle = \beta|\alpha\beta\rangle, \tag{7.58}$$

[1] This choice is not unique and in general there is no constructive way to find the correct operators.

where $\beta = \hbar m$. Since the eigenvalue spectrum of L_z is equidistant (see section 7.3), it should be possible to define raising and lowering operators L_+, L_-, which are independent of quantum number m.

Harmonic oscillator	Angular momentum
$[a^\dagger a, a^\dagger] = a^\dagger$ $[a^\dagger a, a] = -a$	$[L_z, L_\pm] = \pm\hbar L_\pm$
$a^\dagger, a$ result in raising/lowering n	$L_\pm$ raises/lowers the quantum number β by one unit of $\hbar$ (see (7.59) and (7.60))

$$L_z L_+|\alpha\beta\rangle = (L_+ L_z + \hbar L_+)|\alpha\beta\rangle = (\beta + \hbar) L_+|\alpha\beta\rangle \tag{7.59}$$

$$L_z L_-|\alpha\beta\rangle = (L_- L_z - \hbar L_-)|\alpha\beta\rangle = (\beta - \hbar) L_-|\alpha\beta\rangle \tag{7.60}$$

The commutation rule

$$\boxed{[L_z, L_\pm] = \pm\hbar L_\pm} \tag{7.61}$$

is fulfilled by the definition

$$\boxed{L_\pm = L_x \pm i L_y}. \tag{7.62}$$

$L_\pm$ is called the raising/lowering operator. Since $[\vec{L}^{\,2}, L_i] = 0$, $i = x, y, z$ yields, the following commutation rule is valid,

$$\boxed{[\vec{L}^{\,2}, L_\pm] = 0}. \tag{7.63}$$

It follows that the raising/lowering operators leave the eigenvalue α of $\vec{L}^{\,2}$ unchanged, i.e.

$$\vec{L}^{\,2} L_\pm|\alpha\beta\rangle = \alpha L_\pm|\alpha\beta\rangle\ . \tag{7.64}$$

Eigenvalue of L_z ($\alpha, \beta \in \mathbb{R}$):

$$L_\pm|\alpha\beta\rangle = C_\pm(\alpha, \beta)|\alpha, \beta \pm \hbar\rangle, \tag{7.65}$$

which represents a ladder of equidistant eigenvalues.

- **Classical:**
  Component $|L_z|$ should not be larger than the length $|\vec{L}|$.

- **Quantum mechanical:**

$$\langle\alpha\beta|L^2 - L_z^2|\alpha\beta\rangle = \langle\alpha\beta|(\alpha - \beta^2)|\alpha\beta\rangle \tag{7.66}$$

$$\langle\alpha\beta|(L_x^2 + L_y^2)|\alpha\beta\rangle \geq 0, \tag{7.67}$$

  since L_x^2, L_y^2 are positive definite. Equation (7.67) is equivalent to

$$\beta^2 \leq \alpha \qquad -\sqrt{\alpha} \leq \beta \leq \sqrt{\alpha}, \tag{7.68}$$

  like in the classical case.

Therefore there exists a maximum (minimum) eigenvalue $\beta_{\max}$, $\beta_{\min}$ which cannot be raised (lowered), i.e.

$$L_+|\alpha\beta_{\max}\rangle = 0 \qquad \text{and} \qquad L_-|\alpha\beta_{\min}\rangle = 0. \tag{7.69}$$

Relations between α and $\beta_{\max}$, $\beta_{\min}$

$$L_-L_+ = (L_x - iL_y)(L_x + iL_y) \tag{7.70}$$

$$= L^2 - L_z^2 - \hbar L_z \tag{7.71}$$

$$0 = L_-L_+|\alpha\beta_{\max}\rangle = (L^2 - L_z^2 - \hbar L_z)|\alpha\beta_{\max}\rangle \tag{7.72}$$

$$= \alpha - \beta_{\max}^2 - \hbar\beta_{\max} \tag{7.73}$$

$$L_+L_- = L^2 - L_z^2 + \hbar L_z \tag{7.74}$$

$$0 = L_+L_-|\alpha\beta_{\min}\rangle = \alpha - \beta_{\min}^2 + \hbar\beta_{\min} \tag{7.75}$$

From equation (7.73) we get the relation

$$\boxed{\alpha = \beta_{\max}(\beta_{\max} + \hbar)} \tag{7.76}$$

and from equation (7.75)

$$\boxed{\alpha = \beta_{\min}(\beta_{\min} - \hbar)} \quad \text{and} \quad \boxed{\beta_{\min} = -\beta_{\max}}. \tag{7.77}$$

Since $|\alpha\beta_{\min}\rangle$ is obtained from $|\alpha\beta_{\max}\rangle$ by applying L_- k-times, $k \in \mathbb{N}_0$ integer, we have

$$\beta_{\max} - \beta_{\min} = 2\beta_{\max} = \hbar k \tag{7.78}$$

and therefore

$$\boxed{\begin{aligned} \beta_{\max} &= \frac{\hbar k}{2} = -\beta_{\min}, \quad k \in \mathbb{N}_0 \\ \alpha &= \hbar^2 \frac{k}{2}\left(\frac{k}{2}+1\right) \end{aligned}} \,. \tag{7.79}$$

Remark:
The solution of the eigenvalue problem of L_z in the representation of scalar wave functions in position space (see section 7.3) has shown that $\beta = \hbar m$ can take on only integer values of $\hbar$.
Our general, representation-free discussion above shows that both integer and half-integer values are allowed. The half-integer values correspond to different representation of the rotation group, acting in the vector space of "spinors", i.e. vector spaces with *even* dimensionality $d = 2, 4$. The integer values occur in representations of the rotation group acting in vector spaces with odd dimensionality, scalar wave function $d = 1$, vector wave function, $d = 3$ etc. In nature, the spinor representations are also realized and correspond to particles with spin, an "internal" quantum degree of freedom without classical analogon (see chapter 9). The more general generators of the rotation group with integer or half-integer eigenvalues are usually denoted by J's.

$$\vec{L} \longrightarrow \vec{J}, \qquad L_\pm \longrightarrow J_\pm \tag{7.80}$$

Summary of results: Rename $\frac{k}{2} \to j$

$$\boxed{\begin{aligned} \vec{J}^2|j\,m\rangle &= j(j+1)\hbar^2|j\,m\rangle \\ J_z|j\,m\rangle &= m\hbar|j\,m\rangle, \end{aligned}} \tag{7.81}$$

with

$$j = \begin{cases} 0, 1, 2, \ldots \\ \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots \end{cases} \tag{7.82}$$

$$m = j, j-1, \ldots, -j+1, -j \quad \text{for given } j. \tag{7.83}$$

Therefore m can take $(2j+1)$ values. For the angular momentum representation of scalar wave functions in position space, we identify

$$j = l = 0, 1, 2, \ldots \quad \text{(integer)} \tag{7.84}$$
$$m = l, l-1, \ldots, -l\ . \tag{7.85}$$

These eigenstates $|l\, m\rangle$ defined in this way are the only ones possible.

Proof:
The steps of argumentation are analogous to the ones used in the harmonic oscillator problem. The states $|l\, m_{max}\rangle$ and $|l\, m_{min}\rangle$ are unique, because the differential equations in position space corresponding to

$$L_+|l\, m_{max}\rangle = 0 \tag{7.86}$$
$$L_-|l\, m_{min}\rangle = 0 \tag{7.87}$$

have unique solutions, where

$$L_\pm = L_x \pm iL_y \qquad \longrightarrow \qquad \pm\hbar e^{i\varphi}\left(\frac{\partial}{\partial\theta} \pm i\cot(\theta)\frac{\partial}{\partial\varphi}\right), \tag{7.88}$$

where we have used the definition of L_x, L_y in the x-basis.

7.4.2 Full determination of the eigenstates $|j,\, m\rangle$

Once, for given j, the states with maximal or minimal m, $|j,\, j\rangle$ or $|j,\, -j\rangle$, are determined, all other states with the same j-value are obtained by the action of J_+ or J_-.

$$J_\pm|j,\, m\rangle = C_\pm(j,m)|j,\, m \pm 1\rangle, \tag{7.89}$$

but the factors $C_\pm(j,m)$ are still unknown. Now we build the adjoint equation of (7.89),

$$\langle j,\, m|J_\mp = C^*_\pm(j,m)\langle j,\, m \pm 1|, \tag{7.90}$$

and by this obtain

$$\langle j,\, m|J_-J_+|j,\, m\rangle = |C_+(j,m)|^2\langle j\, m+1|j\, m+1\rangle \tag{7.91}$$
$$\Leftrightarrow \langle j,\, m|\left(J^2 - J_z^2 - \hbar J_z\right)|j,\, m\rangle = |C_+(j,m)|^2. \tag{7.92}$$

This yields

$$|C_+(j,m)|^2 = \hbar^2[j(j+1) - m^2 - m] \tag{7.93}$$
$$= \hbar^2(j-m)(j+m+1). \tag{7.94}$$

By convention, we choose the overall phase factor of $C_+(j,m)$, $e^{i\alpha} = 1$ and get

$$C_+(j,m) = \hbar\sqrt{(j-m)(j+m+1)}. \tag{7.95}$$

Similarly, using $\langle j\,m|J_+J_-|j\,m\rangle = |C_(j,m)|^2$, it can be shown that

$$C_-(j,m) = \hbar\sqrt{(j+m)(j-m+1)} \tag{7.96}$$

is valid, i.e.

$$\boxed{J_\pm|j\,m\rangle = \hbar\sqrt{(j\mp m)(j\pm m+1)}|j\,m\pm 1\rangle}. \tag{7.97}$$

7.4.3 Matrix elements of the angular momentum components: Multiplets

$$\langle j'\,m|J_x|j\,m\rangle = \left\langle j'\,m'\left|\frac{J_+ + J_-}{2}\right|j\,m\right\rangle \tag{7.98}$$
$$= \frac{\hbar}{2}\delta_{jj'}\Big[\delta_{m'm+1}\sqrt{(j-m)(j+m+1)} + \delta_{m'm-1}\sqrt{(j+m)(j-m+1)}\Big] \tag{7.99}$$
$$\langle j'\,m'|J_y|j\,m\rangle = \left\langle j'\,m'\left|\frac{J_+ - J_-}{2i}\right|j\,m\right\rangle \tag{7.100}$$
$$= \frac{\hbar}{2i}\delta_{jj'}\Big[\delta_{m'm+1}\sqrt{(j-m)(j+m+1)} - \delta_{m'm-1}\sqrt{(j+m)(j-m+1)}\Big] \tag{7.101}$$
$$\langle j'\,m'|J_z|j\,m\rangle = \delta_{jj'}\delta_{mm'}\hbar m \tag{7.102}$$
$$\langle j'\,m'|\vec{J}^2|j\,m\rangle = \delta_{jj'}\delta_{mm'}\hbar^2 j(j+1) \tag{7.103}$$

Matrix representation

- of $\vec{J}^2/\hbar^2$:

		j	0	1/2		1			
		m	0	1/2	$-1/2$	1	0	-1	
j	m								
0	0		0					0	...
1/2	1/2			3/4	0				
1/2	$-1/2$			0	3/4				
1	1					2	0	0	
1	0					0	2	0	
1	-1		0			0	0	2	
			⋮						

- of $J_x/\hbar$:

		j	0	1/2	1/2	1	1	1	
		m	0	1/2	$-1/2$	1	0	-1	
j	m								
0	0		0					0	...
1/2	1/2			0	1/2				
1/2	$-1/2$			1/2	0				
1	1					0	$1/\sqrt{2}$	0	
1	0					$1/\sqrt{2}$	0	$1/\sqrt{2}$	
1	-1		0			0	$1/\sqrt{2}$	0	
			⋮						

The matrix elements do not vanish only for $m - m' = \pm 1$.

- of $J_y/\hbar$:

		j	0	1/2	1/2	1	1	1	
		m	0	1/2	$-1/2$	1	0	-1	
j	m								
0	0		0					0	...
1/2	1/2			0	$i/2$				
1/2	$-1/2$			$i/2$	0				
1	1					0	$-i/\sqrt{2}$	0	
1	0					$i/\sqrt{2}$	0	$-i/\sqrt{2}$	
1	-1		0			0	$i/\sqrt{2}$	0	
			$\vdots$						

Notice:
J_x, J_y, J_z acting on any state $|j,\, m\rangle$ leave j = constant. In the basis $\{|j,\, m\rangle\}$, the J_x, J_y, J_z matrices have block structure with blocks of j =constant.

- The finite rotation $R(\varphi) = e^{-i\vec{\varphi}\cdot\vec{J}}$ about the axis $\widehat{\varphi}$ by angle $|\vec{\varphi}|$ leaves j =const. and the subspace $V^{(j)}$ spanned by $\{|j,\, j\rangle, \ldots, |j,\, -j\rangle\}$ is therefore invariant under any rotation.

- Any basis state $|j,\, m\rangle$ can be transformed into any other basis state $|j,\, m'\rangle$ *with the same* j by an appropriate rotation, because J_x, J_y are composed of J_+, J_-. Thus there is no invariant subspace of $V^{(j)}$.

- The representation of the angular momentum algebra, or the rotation group, as linear transformations, or rotations, in the $(2j+1)$-dimensional space of angular momentum states $V^{(j)}$ is *irreducible*.

$$D: \quad J_i \longrightarrow D(J_i) = J_i^{(j)} \qquad \text{(irreducible representation)} \qquad (7.104)$$

The upper index (j) indicates that J_i is acting on the j-subspace. The basis set $\{|j,\, j\rangle \ldots |j,\, -j\rangle\}$ is called the j-multiplet of the representation.
The representation of the angular momentum algebra, or rotation group, in a space with several different j (above matrices) is reducible, since it can be decomposed into invariant subspaces.

7.4.4 Angular momentum eigenfunctions in the position basis

$$\psi_l^m(r,\theta,\varphi) = R(r)Y_l^m(\theta,\varphi) \tag{7.105}$$

The eigenfunctions of $\vec{L}^2$, L_z can be determined explicitly in the position basis by

1. determining $\psi_l^{m_{\max}=l}(r,\theta,\varphi) = \langle\vec{x}|l,\, l\rangle$
2. repeatedly acting with L_- on $\psi_l^l(r,\theta,\varphi)$ in the x-basis.

Since $\vec{L}^2$ is in x-basis the angular part of $\vec{\nabla}^2$, $Y_l^m(\theta,\varphi)$ are spherical harmonics.

1. **Eigenfunctions for the case** $m = l$
   We have

$$L_+|l,\, l\rangle = 0 \qquad \text{and} \qquad L_\pm = \pm\hbar e^{\pm i\varphi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\varphi}\right) \tag{7.106}$$

   and therefore get

$$\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)\psi_l^l(r,\theta,\varphi) = 0. \tag{7.107}$$

   We proceed a factorization of the following form

$$\psi_l^l(r,\theta,\varphi) = R(r)Y_l^l(\theta,\varphi), \tag{7.108}$$

   where the radial part $R(r)$ is not determined by the $\vec{L}$ operators. It will be fixed by the radial part of a rotational invariant Hamiltonian. Since equation (7.107) is a sum of terms containing the $\frac{\partial}{\partial\theta}$ or $\frac{\partial}{\partial\varphi}$ differential operators separately, the solution separates in $\theta-$ and $\varphi-$dependent parts,

$$Y_l^l(\theta,\varphi) = U_l^l(\theta)e^{il\varphi}. \tag{7.109}$$

   The exponential factor has the given form since $Y_l^l(\theta,\varphi)$ is eigenfunction of L_z with eigenvalue $l\hbar$. Plugging this ansatz into equation (7.107) one gets a differential equation for $U_l^l(\theta)$,

$$\left(\frac{\partial}{\partial\theta} - l\cot(\theta)\right)U_l^l(\theta) = 0. \tag{7.110}$$

Separation of variables gives

$$\frac{dU}{U} = l\frac{d\sin(\theta)}{\sin(\theta)} \tag{7.111}$$

$$U_l^l(\theta) = (\sin(\theta))^l, \tag{7.112}$$

up to normalization which can be absorbed in R. The normalized eigenfunctions are

$$Y_l^l(\theta,\varphi) = (-1)^l\sqrt{\frac{(2l+1)!}{4\pi}}\frac{1}{2^l l!}(\sin(\theta))^l\ e^{il\varphi} \tag{7.113}$$

$$\int d\Omega \left|Y_l^l(\theta,\varphi)\right|^2 = \int_{-1}^{+1} d\cos(\theta)\int_0^{2\pi} d\varphi \left|Y_l^l(\theta,\varphi)\right|^2 \tag{7.114}$$

$$= 1 \tag{7.115}$$

2. **Eigenfunctions for arbitrary** $l, m \geq 0$

$$Y_l^m(\theta,\varphi) = \frac{1}{\hbar^{l-m}}\frac{1}{\sqrt{(2l)\ldots(l+m+1)}\sqrt{1\ldots(l-m)}}L_-^{l-m}Y_l^l(\theta,\varphi) \tag{7.116}$$

$$\boxed{\begin{aligned} Y_l^m(\theta,\varphi) &= (-1)^l\sqrt{\frac{(2l+1)!}{4\pi}}\frac{1}{2^l l!}\sqrt{\frac{(l+m)!}{(2l)!(l-m)!}}e^{im\varphi} \\ &\quad\times(\sin(\theta))^{-m}\frac{d^{l-m}}{d\cos(\theta)^{l-m}}(\sin(\theta))^{2l}, \quad m\geq 0 \\ Y_l^{-m}(\theta,\varphi) &= (-1)^m\, Y_l^m(\theta,\varphi)^*, \end{aligned}} \tag{7.117}$$

since m occurs in $e^{im\varphi}$ only. The functions $Y_l^m(\theta,\varphi)$ are called spherical harmonics which are normalized and complete by the algebraic construction.

$$\int d\Omega\, Y_l^{m'*}(\theta,\varphi)Y_l^m(\theta,\varphi) = \delta_{ll'}\delta_{mm'} \tag{7.118}$$

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{+l} Y_l^{m*}(\theta',\varphi')Y_l^m(\theta,\varphi) = \delta^2(\Omega-\Omega'), \tag{7.119}$$

where $\Omega = (\theta,\varphi)$.

Any wave function $\psi(r,\theta,\varphi)$ can be expanded in the Y_l^m with r-dependent coefficients,

$$\psi(r,\theta,\varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} R_l^m(r) Y_l^m(\theta,\varphi). \tag{7.120}$$

This will be used in the solution of Hamiltonian eigenvalue problems with spherical symmetry. From orthonormality we get

$$R_l^m(r) = \int d\Omega\, Y_l^{m*}(\theta,\varphi)\psi(r,\theta,\varphi). \tag{7.121}$$

Some spherical harmonics

$$l=0: \quad Y_0^0 = \sqrt{\frac{1}{4\pi}} \tag{7.122}$$

$$l=1: \quad Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin(\theta)e^{\pm i\varphi} \tag{7.123}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos(\theta) \tag{7.124}$$

$$l=2: \quad Y_2^{\pm 2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\varphi} \tag{7.125}$$

$$Y_2^{\pm 1} = \sqrt{\frac{15}{8\pi}}\sin(\theta)\cos(\theta)e^{\pm i\varphi} \tag{7.126}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos(\theta)-1) \tag{7.127}$$

The spherical harmonics are related to the *associated Legendre polynomials* $P_l^m(\cos(\theta))$ via

$$\boxed{Y_l^m(\theta,\varphi) = \sqrt{\tfrac{(2l+1)(l-m)!}{4\pi(l+m)!}}(-1)^m e^{im\varphi} P_l^m(\cos(\theta))}, \tag{7.128}$$

where the $P_l^0 = P_l(\cos(\theta))$ are the Legendre polynomials. Recursion relations for Y_l^m, P_l^m can be proved using their algebraic structure as eigenfunctions of $\vec{L}^2$, L_z. The following 3-dimensional plots[2] show the angle-dependent value of $Y_l^m(\theta,\varphi)$.

[2]Plots available at http://www.vis.uni-stuttgart.de/~kraus/LiveGraphics3D/java_script/SphericalHarmonics.html

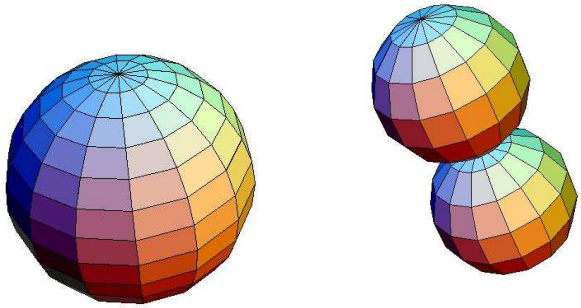

Figure 7.3: Spherical harmonics for $l = 0, m = 0$ and $l = 1, m = 0$

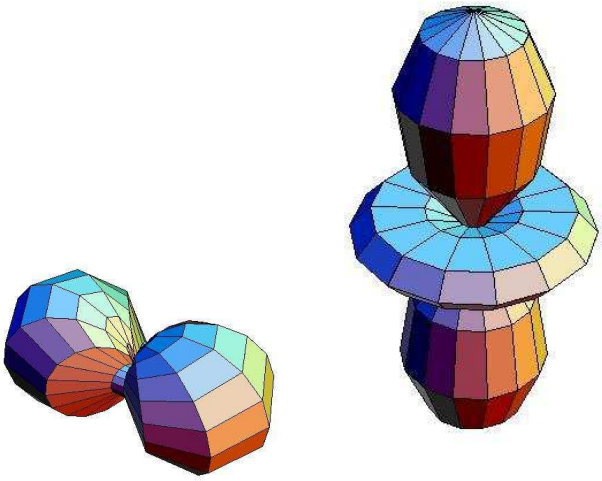

Figure 7.4: Spherical harmonics for $l = 1, m = \pm 1$ and $l = 2, m = 0$

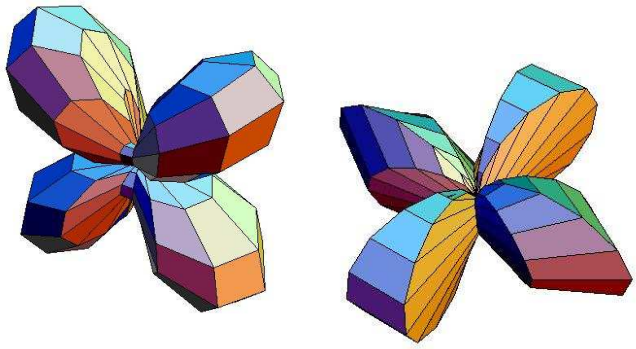

Figure 7.5: Spherical harmonics for $l = 2, m = \pm 1$ and $l = 2, m = \pm 2$

Chapter 8

The Hydrogen Atom

8.1 Solution of rotationally invariant problems: general properties

- **Separation of center-of-mass motion**
  System of 2 particles m_1, m_2, moving in a potential $V(r)$ depending only on the distance $r = |\vec{r}_2 - \vec{r}_1|$ of the particles.

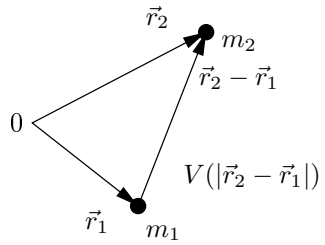

Figure 8.1: Two body problem in a radial-dependent potential

Relative and center-of-mass coordinates:

$$\vec{r} = \vec{r}_2 - \vec{r}_1, \qquad r = |\vec{r}_2 - \vec{r}_1| \tag{8.1}$$

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} \tag{8.2}$$

Separation of free COM motion:

$$-\frac{\hbar^2}{2(m_1+m_2)}\frac{\partial^2}{\partial R^2}\psi_{\mathrm{COM}}(\vec{R}) = E_{\mathrm{COM}}\psi_{\mathrm{COM}}(\vec{R}) \tag{8.3}$$

Relative motion:

Particle of effective mass μ in a central symmetric potential $V(r)$

- **Separation of angular motion: radial Schrödinger equation**

  Kinetic energy in spherical coordinates:

$$\vec{p}^{\,2} = \vec{p}_r{}^{\,2} + \vec{p}_\perp{}^{\,2} = \vec{p}_r{}^{\,2} + \left[\frac{\vec{r}}{r}\times\vec{p}\right]^2, \tag{8.4}$$

  where the second term is the component of $\vec{p}$ which is perpendicular to $\vec{r}$ and therefore unimportant for the squared absolut value.

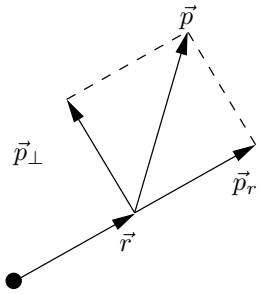

Figure 8.2: Division of $\vec{p}$ into radial and perpendicular part

$$\vec{p}^{\,2} = \vec{p}_r{}^{\,2} + \frac{1}{r^2}\vec{L}^{\,2} \tag{8.5}$$

with

$$\begin{aligned}
\vec{L}^{\,2} &= L_x^2 + L_y^2 + L_z^2 && (8.6)\\
&= -\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] && (8.7)\\
\vec{p}_r{}^{\,2} &= \hbar^2\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}. && (8.8)
\end{aligned}$$

The Schrödinger equation in spherical coordinates therefore reads

$$\begin{aligned}
&\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\vec{L}^{\,2}}{2\mu r^2} + V(r)\right]\psi_{Elm}(r,\theta,\varphi),\\
&= E\psi_{Elm}(r,\theta,\varphi)
\end{aligned} \tag{8.9}$$

where the term $\frac{\vec{L}^2}{2\mu r^2}$ is the centrifugal potential. Since the Hamilton operator H is a sum of purely radial and angular derivative terms, the solution separates into radial and angular parts, with the angular part being an eigenfunction of $\vec{L}^2$.

$$\psi_{Elm}(r,\theta,\varphi) = R_{El}Y_l^m(\theta,\varphi) \tag{8.10}$$

Degeneracy of the solutions

Since H does not depend on L_z, the ψ_{Elm} must be degenerate with respect to m. By $[H, L_\pm] = 0$ we obtain

$$\begin{aligned} H\psi_{Elm} &= E\psi_{Elm} && (8.11)\\ \Leftrightarrow HL_\pm\psi_{Elm} &= EL_\pm\psi_{Elm} && (8.12)\\ \Leftrightarrow H\psi_{Elm\pm1} &= E\psi_{Elm\pm1}. && (8.13) \end{aligned}$$

The square of the angular momentum operator reads in spherical coordinates

$$\begin{aligned} \vec{L}^2 &= L_x^2 + L_y^2 + L_z^2 && (8.14)\\ &= -\hbar^2\left[\left(\sin(\varphi)\frac{\partial}{\partial\theta} + \cos(\varphi)\cot\theta\frac{\partial}{\partial\varphi}\right)^2\right.\\ &\quad \left. + \left(-\cos(\varphi)\frac{\partial}{\partial\theta} + \sin(\varphi)\cot\theta\frac{\partial}{\partial\varphi}\right)^2 + \frac{\partial^2}{\partial\varphi^2}\right] && (8.15)\\ &= -\hbar^2\left[\sin^2\varphi\frac{\partial^2}{\partial\theta^2} + \cot^2\theta\left(\cos(\varphi)\frac{\partial}{\partial\varphi}\cos(\varphi)\frac{\partial}{\partial\varphi}\right)\right.\\ &\quad + \sin(\varphi)\frac{\partial}{\partial\theta}\cos(\varphi)\cot\theta\frac{\partial}{\partial\varphi} + \cos(\varphi)\cot\theta\frac{\partial}{\partial\varphi}\sin(\varphi)\frac{\partial}{\partial\theta}\\ &\quad + \cos^2\varphi\frac{\partial^2}{\partial\theta^2} + \cot^2\theta\left(\sin(\varphi)\frac{\partial}{\partial\varphi}\sin(\varphi)\frac{\partial}{\partial\varphi}\right)\\ &\quad - \cos(\varphi)\frac{\partial}{\partial\theta}\sin(\varphi)\cot\theta\frac{\partial}{\partial\varphi} - \sin(\varphi)\cot\theta\frac{\partial}{\partial\varphi}\cos(\varphi)\frac{\partial}{\partial\theta}\\ &\quad \left. + \frac{\partial^2}{\partial\varphi^2}\right] && (8.16)\\ &= -\hbar^2\left[\frac{\partial^2}{\partial\theta^2} + \cot^2\theta\frac{\partial^2}{\partial\varphi^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{\partial^2}{\partial\varphi^2}\right] && (8.17)\\ &= -\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]. && (8.18) \end{aligned}$$

Radial part of the Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r^2}r^2\frac{\partial}{\partial r}+\frac{\hbar^2 l(l+1)}{2\mu r^2}+V(r)\right]R_{El}(r) \tag{8.19}$$

$$= \left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{d}{dr}\right)+\frac{\hbar^2 l(l+1)}{2\mu r^2}+V(r)\right]R_{El}(r) \tag{8.20}$$

$$= ER_{El}(r), \tag{8.21}$$

since

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\left(\frac{1}{r}U(r)\right) \tag{8.22}$$

$$= -\frac{1}{r^2}\frac{\partial}{\partial r}U(r)+\frac{1}{r^2}\frac{\partial}{\partial r}r\frac{d}{dr}U(r) \tag{8.23}$$

$$= -\frac{1}{r^2}\frac{\partial}{\partial r}U+\frac{1}{r^2}\frac{\partial}{\partial r}U+\frac{1}{r}\frac{d^2}{dr^2}U. \tag{8.24}$$

We define $R_{El}(r) =: \frac{1}{r}U_{El}(r)$ and then obtain

$$\boxed{\left[\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-\frac{2\mu}{\hbar^2}V(r)\right]U_{El}(r)=-\frac{2\mu E}{\hbar^2}U_{El}(r)}. \tag{8.25}$$

This equation is similar to 1the one-dimensional Schrödinger equation, but

- repulsive centrifugal potential $\sim \frac{l(l+1)}{r^2}$,
- $0 \leq r \leq \infty$.

We therefore have to take boundary conditions for $r \to \infty$ and $r = 0$ into account.

- **Limiting behavior of $U_{El}(r)$ for $r \to \infty$**
  The central potential shall be localized, i.e. $V(r) \to 0$ for the case $r \to \infty$. We then get two types of solutions, a bound state for $U_{El} \to 0$ and a scattering states which is unbound and asymptotically free for $U_{El} \sim e^{\pm ikr}$. The scattering states will be considered in a later chapter (Scattering theory). Hence, we will consider only bound states.

- **Boundary condition for $r \to 0$**
  We assume that $V(r)$ is less singular than $\frac{1}{r^2}$ for $r \to 0$, because otherwise

the problem would be dominated by $V(r)$ for $r \to 0$, and the $r \to 0$ solution would depend on the details of $V(r)$. The radial Schrödinger equation in the limit $r \to 0$ reads

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2}\right] U_{El}(r) = 0. \tag{8.26}$$

We make the ansatz

$$U \sim r^{\alpha}, \tag{8.27}$$

with

$$\alpha(\alpha - 1) = l(l+1) \tag{8.28}$$

$$\alpha = \begin{cases} l+1 \\ -l \end{cases} \tag{8.29}$$

$$U_l(r) \sim \begin{cases} r^{l+1} & \text{(regular)} \\ r^{-l} & \text{(irregular)} \end{cases} . \tag{8.30}$$

Note:
These two types of asymptotic solutions are the only ones possible, since a differential equation of second order has two linearly independent solutions. The irregular solution r^{-l} is excluded on physical grounds, or precisely because of normalizability.

$$\int_0^{R_0} dr\, r^2 r^{-2(l+1)} = \int_0^{R_0} dr\, r^2 |R(r)|^2 < \infty \tag{8.31}$$

only for $l = 0, 1, \ldots$ because the probability density $|R(r)|^2 \sim |r^{-(l+1)}|^2$ would otherwise diverge.

8.2 The hydrogen atom

8.2.1 The energy eigenvalues

The effective mass μ is defined by

$$\mu = \frac{m_p m_e}{m_p + m_e} \approx m_p \equiv m, \tag{8.32}$$

where m_p is the proton mass and m_e the electron mass which are in the ratio $m_p/m_e \approx 2000$. The radial Schrödinger equation was given by

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - \frac{2\mu}{\hbar^2}(V(r) - E)\right] U_{El}(r) = 0, \tag{8.33}$$

where $V(r)$ is in this case the Coulomb potential,

$$V(r) = -\frac{e^2}{r}. \tag{8.34}$$

In this chapter we will only consider solutions with $E < 0$. The region with $E < V(r)$, i.e. $r > \frac{e^2}{-E}$, is classically forbidden, so that we expect exponentially decaying solutions for $r \to \infty$. In the following we want to derive the bound states of the system.

For

$$\frac{e^2}{r} \ll |E|, \quad \frac{\hbar^2 l(l+1)}{2\mu r^2} \ll |E| \tag{8.35}$$

we have

$$\left(\frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2}E\right) U_{El} = 0 \tag{8.36}$$

$$U_{El}(r) \sim e^{-\kappa r} \quad (r \to \infty) \tag{8.37}$$

$$U_{El}(r) \sim r^{l+1} \quad (r \to 0), \tag{8.38}$$

where

$$\kappa = \frac{\sqrt{-2\mu E}}{\hbar}. \tag{8.39}$$

Now we introduce the natural dimensionless variable ϱ, defined by

$$\boxed{\varrho = \kappa r = \frac{\sqrt{2\mu|E|}}{\hbar} r}. \tag{8.40}$$

The quantized binding energy $|E|$ will be determined by the boundary conditions, like in any bound state problem.

We make a power series ansatz for $U_{El}(r)$,

$$U_{El}(r) = v_{El}(\varrho)e^{-\varrho} \tag{8.41}$$

$$v_{El}(\varrho) = \varrho^{l+1}\sum_{k=0}^{\infty} C_k \varrho^k. \tag{8.42}$$

Plugging this ansatz into equation (8.33) yields

$$\frac{d^2v}{d\varrho^2} - 2\frac{dv}{d\varrho} + \left[\frac{e^2\lambda}{\varrho} - \frac{l(l+1)}{\varrho^2}\right] v = 0, \tag{8.43}$$

with

$$\lambda := \sqrt{\frac{2\mu}{\hbar^2|E|}}. \tag{8.44}$$

Using the power series ansatz (8.42), analogous to the harmonic oscillator, gives

$$\begin{aligned} 0 &= \sum_{k=0}^{\infty} \Big\{ C_k \left[(k+l+1)(k+l) - l(l+1)\right] \varrho^{k+l-1} \\ &\quad C_k \left[-2(k+l+1) + e^2\lambda\right] \varrho^{k+l} \Big\} \qquad (8.45) \\ &= \sum_{k=0}^{\infty} \Big\{ C_{k+1} \left[(k+l+2)(k+l+1) - l(l+1)\right] \\ &\quad + C_K \left[-2(k+l+1) + e^2\lambda\right] \Big\} \varrho^{k+l} \qquad (8.46) \end{aligned}$$

By this we get the recursion relation

$$\boxed{c_{k+1} = c_k \frac{-e^2\lambda + 2(k+l+1)}{(k+l+2)(k+l+1) - l(l+1)}}. \tag{8.47}$$

Note:
For the one-dimensional harmonic oscillator there is a 2-step recursion relation, leading to a purely even or odd power series, reflecting parity eigenfunction. For the three-dimensional problem of the H-atom, the parity operation $\varphi \to \varphi + \pi$, $\theta \to \pi - \theta$, is not reflected in r. Therefore, the power series in r has no definite parity here.

In the limit $k \to \infty$ we get

$$c_{k+1} = \frac{2}{k} c_k \quad \longrightarrow \quad \sum_{k \gg 0}^{\infty} \frac{1}{k!} (2\varrho)^k = A + e^{2\varrho}. \tag{8.48}$$

An infinite series would lead to diverging solution, so that the series must terminate at some finite k for which $c_{k+1} = 0$ is valid.

$$e^2 \lambda = 2(k + l + 1) \tag{8.49}$$

or

$$E = -\frac{\mu e^4}{2\hbar^2 (k + l + 1)^2}, \tag{8.50}$$

with

$$k = 0, 1, 2, \ldots \tag{8.51}$$

$$l = 0, 1, 2, \ldots. \tag{8.52}$$

From this we can see that the energy eigenvalue is quantized. Since E depends only on $n = k + l + 1$, we can choose n as the relevant quantum number, i.e.

$$E_n = -\frac{\mu e^4}{2\hbar^2} \frac{1}{n^2}, \tag{8.53}$$

where the factor $\mu e^4 / 2\hbar^2$ is known as the *Rydberg*-unit which has the numerical value

$$1\,\mathrm{Ry} \cong 13,6\mathrm{eV}. \tag{8.54}$$

8.2.2 Degeneracy of the energy states n

1. The energy eigenvalue E_n does not depend on the magnetic quantum number m for the following reasons.

$$[H, L_{x,y,z}] = 0 \qquad \text{(rotational invariance)} \tag{8.55}$$

$$[H, L_{\pm}] = 0 \tag{8.56}$$

$$H\psi_n = E_n \psi_n \tag{8.57}$$

$$\Rightarrow H L_{\pm} \psi_n = E_n L_{\pm} \psi_n \,. \tag{8.58}$$

Therefore we have degenerate multiplets of states, i.e. that the energy eigenvalue E_n has for given n, l the same value for

$$m = l, l-1, \ldots, -l, \tag{8.59}$$

so that each state (n, l) is $(2l+1)$-fold degenerate.

2. The energy eigenvalue E_n does not depend on l, although the radial Schrödinger equation does.

   There is another raising/lowering operator $M_\pm$ which increases/lowers $l \to l \pm 1$, with $[H, M_\pm] = 0$, i.e. $M_\pm$ are the generators of another, hidden, symmetry group. It is related to the conserved Runge-Lenz vector in classical mechanics. This degeneracy is a speciality of the Coulomb $\frac{1}{r}$-potential ("accidental symmetry").
   For other potentials the recursion relation would be more complicated, involving more than 2 c_k's, and E would depend on n, l.

3. For given n the angular momentum quantum number l takes the values

   $$l = 0, 1, \ldots, n-1, \tag{8.60}$$

   and for fixed $k = n - l - 1$ the magnetic quantum number takes the values

   $$m = +l, \ldots, -l. \tag{8.61}$$

   Total degeneracy of an energylevel E_n

   $$\boxed{\sum_{l=0}^{n-1}(2l+1) = 2 \cdot \frac{1}{2}(n-1)n + n = n^2} \tag{8.62}$$

   Hydrogen energy spectrum and spectroscopic terms

8.2.3 The hydrogen eigenfunctions: summary

The eigenfunctions were given by

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_l^m(\theta, \varphi), \tag{8.63}$$

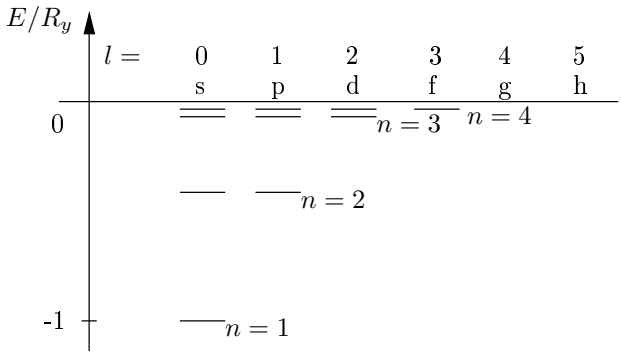

Figure 8.3: Energy spectrum of the hydrogen atom

and the energy eigenvalues by

$$\boxed{E_n = -\frac{\mu e^4}{2\hbar^2}\frac{1}{n^2}}, \tag{8.64}$$

where the principal quantum number takes the values $n = 1, 2, 3, \ldots$. The radial solution was given by

$$\boxed{\begin{aligned} R_{nl}(r) &= \frac{1}{\varrho}U_{nl}(\varrho) = \varrho^l \sum_{k=0}^{n-l-1} c_k \varrho^k e^{-\varrho} \\ c_{k+1} &= c_k \frac{-e^2\lambda + 2(k+l+1)}{(k+l+2)(k+l+1) - l(l+1)} \end{aligned}}, \tag{8.65}$$

where the starting coefficient c_0 is determined by normalization. Furthermore we had introduced the following shorthand notations,

$$\kappa = \sqrt{\frac{2\mu|E|}{\hbar^2}} \tag{8.66}$$

and

$$\varrho = \frac{\mu e^2}{\hbar^2}\frac{1}{n}r = \frac{1}{n}\frac{r}{a_0}, \tag{8.67}$$

with

$$\boxed{a_0 = \frac{\hbar^2}{\mu e^2} \approx 0.55\text{A}}, \tag{8.68}$$

which describes the Bohr radius which again is related to the characteristic "size" of the H-atom. Another representation of the radial solution was derived as

$$R_{nl}(r) = L_{n-l-1}^{2l+1}\left(2\frac{r}{na_0}\right)e^{-\frac{r}{na_0}} \tag{8.69}$$

with

$$L_{n-l-1}^{2l+1}(2\varrho) = \varrho^l \sum_{k=0}^{n-l-1} c_k \varrho^k \tag{8.70}$$

being the Laguerre polynomials, which are defined by a differential equation or by a recursion relation for c_k. Summarizing these results we write down some of the eigenfunctions explicitly as follows,

$$\psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-\frac{r}{a_0}} \tag{8.71}$$

$$\psi_{200} = \left(\frac{1}{32\pi a_0^3}\right)^{\frac{1}{2}} \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \tag{8.72}$$

$$\psi_{210} = \left(\frac{1}{32\pi a_0^3}\right)^{\frac{1}{2}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \cos(\theta) \tag{8.73}$$

$$\psi_{21\pm1} = \mp\left(\frac{1}{64\pi a_0^3}\right)^{\frac{1}{2}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \sin(\theta) e^{\pm i\varphi} \tag{8.74}$$

etc.

Chapter 9

Spin and Magnetic Moment

9.1 Spin and $SU(2)$

In chapter 7 we have found the irreducible representations of the rotation group. They correspond to the rotations R in the space spanned by the angular momentum eigenstates $|j,\, m\rangle$ with fixed j, e.g. J_x in the eigenbasis $|j,\, m\rangle$.

Irreducible representation of the rotation group

		j	0	1/2	1/2	1	1	1	
		m	0	1/2	$-1/2$	1	0	-1	
j	m								
0	0		0					0	...
1/2	1/2			0	1/2				
1/2	$-1/2$			1/2	0				
1	1					0	$1/\sqrt{2}$	0	
1	0					$1/\sqrt{2}$	0	$1/\sqrt{2}$	
1	-1		0			0	$1/\sqrt{2}$	0	
			$\vdots$						

1. $SO(3)$
   If the eigenstates $|j,\, m\rangle$ are taken in the $\vec{x}$-basis, then these transformations

are the rotations of the wave functions in position space, and j can, by construction, only assume integer values, $j = l$ (see chapter 7).

$$\begin{aligned} \langle \vec{x} | l\, m \rangle &= Y_l^m(\widehat{\Omega}) && (9.1) \\ \langle \vec{x} | R(\vec{\alpha}) | l\, m \rangle &= Y_l^m(R^{-1}(\vec{\alpha})\widehat{\Omega}) && (9.2) \\ R(\vec{\alpha}) &= \exp\left(-i\vec{\alpha}\frac{\vec{L}}{\hbar}\right), && (9.3) \end{aligned}$$

with

$$\widehat{\Omega} = (\theta, \varphi), \quad j = l = 0, 1, 2, \ldots. \tag{9.4}$$

The rotation group is the **S**pecial **O**rthogonal group with 3 (real) symmetric generators, called $SO(3)$, with

$$\det R = 1, \qquad ||v\rangle| = \text{const.} \tag{9.5}$$

2. $SU(2)$
The eigenstates $|j,\, m\rangle$ can also be in an abstract vector space, without relation to $\vec{x}$-dependent function. Then half-integer and integer values of j are allowed, corresponding to even- and odd-dimensional representations.

- **2-dimensional representation:** $j = \frac{1}{2}, m = \pm\frac{1}{2}$
We have explicitly calculated the generators in the 2-dimensional J^2, J_z eigenbasis:

$$J_k = \frac{1}{2}\hbar\sigma_k, \qquad k = x, y, z, \tag{9.6}$$

where

$$\boxed{\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}} \tag{9.7}$$

are the *Pauli matrices*, which can be combined as a vector like $\vec{\sigma} = (\sigma_x,\, \sigma_y,\, \sigma_z)^T$.

Properties of the Pauli matrices

(a) $\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \mathbb{1}$

(b) $\sigma_x\sigma_y = i\sigma_z, \quad \sigma_z\sigma_x = i\sigma_y, \quad \sigma_y\sigma_z = i\sigma_x$

(c) $[\sigma_x, \sigma_y] = 2i\sigma_z, \quad [\sigma_z, \sigma_x] = 2i\sigma_y, \quad [\sigma_y, \sigma_z] = 2i\sigma_x$

The general rotation operator in the $|\frac{1}{2}, m\rangle$ basis is:

$$\begin{aligned} U(\vec{\alpha}) &= \exp\left(-i\frac{1}{2}(\vec{\alpha}\cdot\vec{\sigma})\right) && (9.8)\\ &= \sum_{n=0}^{\infty}\frac{1}{n!}\left(-i\frac{1}{2}\vec{\alpha}\vec{\sigma}\right)^n && (9.9)\\ &= \cos(\alpha/2) - i\sin(\alpha/2)(\widehat{\alpha}\cdot\vec{\sigma}), && (9.10)\end{aligned}$$

where $\vec{\alpha}$ represents the rotation axis and angle since,

$$\begin{aligned} \vec{\alpha}\cdot\vec{\sigma} &= \alpha_x\sigma_x + \alpha_y\sigma_y + \alpha_z\sigma_z && (9.11)\\ (\vec{\alpha}\cdot\vec{\sigma})^2 &= \alpha_x^2 I - i\alpha_y\alpha_x\sigma_z + i\alpha_z\alpha_x\sigma_y \\ &\quad + i\alpha_x\alpha_y\sigma_z + \alpha_y^2 I - i\alpha_z\alpha_y\sigma_x \\ &\quad - i\alpha_x\alpha_z\sigma_y + i\alpha_y\alpha_z\sigma_x + \alpha_z^2 I && (9.12)\\ &= |\vec{\alpha}|^2 I && (9.13)\\ (\vec{\alpha}\cdot\vec{\sigma})^{2n} &= |\vec{\alpha}|^{2n} I && (9.14)\\ (\vec{\alpha}\cdot\vec{\sigma})^{2n+1} &= |\vec{\alpha}|^{2n+1}(\widehat{\alpha}\cdot\vec{\sigma}) && (9.15)\end{aligned}$$

The rotation group is the **S**pecial **U**nitary group with 2 (complex hermitean) generators, called $SU(2)$, with

$$\det U = 1, \quad ||v\rangle| = const. \tag{9.16}$$

The generators explicitly read

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \begin{pmatrix} o & u^* \\ u & 0 \end{pmatrix}. \tag{9.17}$$

By construction $SU(2)$ and $SO(3)$ have the same Lie algebra, the angular momentum algebra. There is a group homomorphism, which maps each element of $SU(2)$ to an element of SO(3):

$$\begin{aligned} h: \quad SU(2) &\longrightarrow SO(3) && (9.18)\\ U(\vec{\alpha}) &\longrightarrow R(\vec{\alpha}) && (9.19)\end{aligned}$$

The mapping is defined by the following properties.

(a) $U(\vec{\alpha})$ is an arbitrary $SU(2)$ transformation in the 2-dimensional space spanned by $\{|\frac{1}{2}, m = \pm\frac{1}{2}\rangle\}$

(b) $U(\vec{\alpha})$ transforms the Pauli matrices in such a way that any vector in the 3-dimensional space spanned by σ_x, σ_y, σ_z,

$$\sigma(\vec{b}) := b_x\sigma_x + b_y\sigma_y + b_z\sigma_z \tag{9.20}$$

is rotated by $R(\vec{\alpha})$. The Pauli matrices can be seen as cartesian basis vectors of a 3-dimensional vector space.

Proof:

By components we get

$$U(\alpha\widehat{e}_z)\sigma_x U^\dagger(\alpha\widehat{e}_z) = \cos(\alpha)\sigma_x + \sin(\alpha)\sigma_y \tag{9.21}$$

$$U(\alpha\widehat{e}_z)\sigma_y U^\dagger(\alpha\widehat{e}_z) = \cos(\alpha)\sigma_y - \sin(\alpha)\sigma_x \tag{9.22}$$

$$U(\alpha\widehat{e}_z)\sigma_z U^\dagger(\alpha\widehat{e}_z) = \sigma_z \qquad \text{etc.}, \tag{9.23}$$

since

$$\begin{aligned}
& [\cos(\alpha/2) - i\sin(\alpha/2)\sigma_z]\sigma_x \cdot [\cos(\alpha/2) + i\sin(\alpha/2)\sigma_z] \\
= \; & [\cos(\alpha/2) - i\sin(\alpha/2)\sigma_z] \cdot [\cos(\alpha/2)\sigma_x + i\sin(\alpha/2)\sigma_x\sigma_z] \\
= \; & [\cos(\alpha/2) - i\sin(\alpha/2)\sigma_z] \cdot [\cos(\alpha/2)\sigma_x + \sin(\alpha/2)\sigma_y] \\
= \; & \cos^2(\alpha/2)\sigma_x + 2\sin(\alpha/2)\cos(\alpha/2)\sigma_y - \sin^2(\alpha/2)\sigma_x \\
= \; & \{[\cos(\alpha)\sigma_x + \sin(\alpha)\sigma_y] \cdot [\cos(\alpha/2) - i\sin(\alpha/2)\sigma_z]\}\sigma_y \\
& \times[\cos(\alpha/2) + i\sin(\alpha/2)\sigma_z] \\
= \; & \{\ldots\}[\cos(\alpha/2)\sigma_y - \sin(\alpha/2)\sigma_x] \\
= \; & \cos^2(\alpha/2)\sigma_y - 2\sin(\alpha/2)\cos(\alpha/2)\sigma_x - \sin^2(\alpha/2)\sigma_y \\
= \; & \cos(\alpha)\sigma_y - \sin(\alpha)\sigma_x \quad \text{etc.}
\end{aligned}$$

Furthermore we can follow that

$$U \in SU(2) \quad \Leftrightarrow \quad -U \in SU(2), \tag{9.24}$$

since

$$\det(-U) = 1 \tag{9.25}$$

in the 2-dimensional representation, and

$$h(U) = R \quad \Leftrightarrow \quad h(-U) = R \tag{9.26}$$

yield. Therefore for each $R(\vec{\alpha}) \in SO(3)$ there are exactly 2 elements $\pm U(\vec{\alpha})$, which are mapped onto $R(\vec{\alpha})$ by h.

But $+U(\vec{\alpha})$ and $-U(\vec{\alpha})$ are equivalent,

$$U(\vec{\alpha}) = \cos\left(\frac{\alpha}{2}\right) I - i \sin\left(\frac{\alpha}{2}\right) (\widehat{\alpha} \cdot \vec{\sigma}) \tag{9.27}$$

$$-U(\vec{\alpha}) = \cos\left(\frac{\alpha + 2\pi}{2}\right) I - i \sin\left(\frac{\alpha + 2\pi}{2}\right) (\widehat{\alpha} \cdot \vec{\sigma}). \tag{9.28}$$

Physical meaning:
of the abstract Hilbert space spanned by $\{|j = s = \frac{1}{2},\, m = \pm\frac{1}{2}\rangle\}$.

(a) $s = \frac{1}{2}$ is an allowed representation of the rotation group.

(b) $m = \pm\frac{1}{2}$ is realized in nature as an *internal*, *abstract* degree of freedom of certain particles (electrons, protons, quarks,...)

(c) It has no classical analogon.

(d) Since the $|\frac{1}{2},\, \pm\frac{1}{2}\rangle$ state transforms according to the rotation group $SU(2)$, $s = \frac{1}{2}$, $m = \pm\frac{1}{2}$ is best visualized as an internal angular momentum of the particle, and is called *spin* of the particle.

(e) However, the analogy is not complete because of the half-integer value $j = \frac{1}{2}\hbar$ and the spin eigenvalue of $\vec{J}^2$, $s = \frac{1}{2}$, which cannot be changed in contrast to the orbital angular momentum l. $s = \frac{1}{2}$ is therefore a quantum number characteristic for the particle, like mass or charge, or $|\frac{1}{2},\, \uparrow\rangle$, $|\frac{1}{2},\, \downarrow\rangle$.

(f) The vectors in the $\{|\frac{1}{2},\, \pm\frac{1}{2}\rangle\}$-space are called *spinors*,

$$\begin{pmatrix} \psi_\uparrow(\vec{r}) \\ \psi_\downarrow(\vec{r}) \end{pmatrix}, \tag{9.29}$$

where the $\vec{r}$-dependence not necesary.

- **3-dimensional representation of $SU(2)$:** $s = 1$**,** $m = 0, \pm 1$
  The $j = l = 1$ representation is realized by the rotation of wave functions $Y_l^m(\theta, \varphi)$. It can also be realized as a 3-dimensional representation of $SU(2)$, acting on a 3-dimensional spinor space,

$$\begin{pmatrix} \psi_1(\vec{r}) \\ \psi_0(\vec{r}) \\ \psi_{-1}(\vec{r}) \end{pmatrix}, \qquad s = 1, \quad m_s = 1, 0, -1 \tag{9.30}$$

The 3-components are not identified with the orbital angular momentum m, but with the internal m_s.

Generators (see chapter 7)

$$S_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{9.31}$$

$$S_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \tag{9.32}$$

$$S_z = \hbar \begin{pmatrix} 1 & & \\ & 0 & \\ & & -1 \end{pmatrix} \tag{9.33}$$

Note:
These matrices do not span all 3-dimensional hermitean matrices. There also exists an alternative basis for the generators.

The 3-dimensional representations of $SU(2)$ are the rotations acting on vectors (or vector fields) in 3-dimensional space. The most prominent examples of vector fields are gauge fields $\vec{A}$,

$$\left(\vec{p} - \frac{e}{c}\vec{A}\right), \tag{9.34}$$

in particular the electromagnetic vector potential $\vec{A}$. The time component ϕ of the 4-vector A^μ is not relevant here, since we consider only rotations in position space. All vector fields carry a spin $s = 1$, $m_s = 1, 0, -1$, as an internal degree of freedom, in addition to angular momentum.

Examples:

(a) Gauge fields

(b) Photons, particles of the electromagnetic field, which have spin 1.

9.2 Magnetic moment

When a magnetic field $\vec{B}$ is present in a system, we can calculate from the Schrödinger equation, how the angular momentum $\vec{L}$ couples to $\vec{B}$ and hence, what is the magnetic moment $\vec{M}$ related to $\vec{L}$. In this case the Schrödinger equation reads

$$\left[\frac{1}{2m}\left(\vec{p}-\frac{-e}{c}\vec{A}\right)^2+V(r)\right]\psi(\vec{r})=E\psi(\vec{r}), \tag{9.35}$$

where $-e$ is the elctron charge. Now we consider the kinetic term and derive the squared brackets.

$$\begin{aligned}\left(\vec{p}-\frac{-e}{c}\vec{A}\right)^2 &= \vec{p}^{\,2}+\frac{e}{c}\vec{p}\vec{A}+\frac{e}{c}\vec{A}\vec{p}+\left(\frac{e}{c}\right)^2\vec{A}^{\,2} &(9.36)\\ &= \vec{p}^{\,2}+\frac{e}{c}\left[-i\hbar\vec{\nabla}\cdot\vec{A}+\vec{A}\cdot\vec{p}\right]\\ &\quad +\frac{e}{c}\vec{A}\vec{p}+\left(\frac{e}{c}\right)^2\vec{A}^{\,2} &(9.37)\\ &\cong \vec{p}^{\,2}+2\frac{e}{c}\vec{A}\vec{p}, &(9.38)\end{aligned}$$

where the quadratic term in $\vec{A}$ is neglected for small $\vec{A}$.

$$\vec{B}=[\vec{\nabla}\times\vec{A}] \quad \Rightarrow \quad \vec{A}=-\frac{1}{2}\left[\vec{r}\times\vec{B}\right], \tag{9.39}$$

for $\vec{B}$ =const. on a scale of $\psi(\vec{r})$. We then get

$$\begin{aligned}\vec{A}\vec{p} &= -\frac{1}{2}[\vec{r}\times\vec{B}]\vec{p} &(9.40)\\ &= \frac{1}{2}\vec{B}[\vec{r}\times\vec{p}] &(9.41)\\ &= \frac{1}{2}\vec{B}\vec{L} &(9.42)\end{aligned}$$

and by this obtain

$$\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{\vec{L}^{\,2}}{2mr^2}-\frac{-e}{2mc}\vec{B}\vec{L}+V(r)\right]\psi(\vec{r})=R\psi(\vec{r}), \tag{9.43}$$

with

$$\frac{e}{2mc}\vec{B}\vec{L}=\vec{B}\cdot\vec{M}. \tag{9.44}$$

- Since the energy of a magnetic moment $\vec{M}$ in a $\vec{B}$-field is given by $V = -\vec{B}\vec{M}$, we assign the magnetic moment,

$$\vec{M} = \frac{e\hbar}{2mc}\frac{\vec{L}}{\hbar} = \mu_B \frac{\vec{L}}{\hbar}, \tag{9.45}$$

to the angular momentum $\vec{L}$. Furthermore we define

$$\boxed{\mu_B := \frac{e\hbar}{2mc} = 0.58 \cdot 10^{-8}\frac{eV}{G}} \tag{9.46}$$

as the *Bohr magneton*.

- **Magnetic moment of spin**

At the present state of our theoretical development it is not obvious that a magnetic moment is connected with the internal spin degree of freedom.

When quantum mechanics is formulated in a relativistically invariant way (QMII, Relativistic quantum mechanics), the *existence of spin*, its value for electrons, $s = \frac{1}{2}$, and its magnetic moment follow as a necessary consequence.

The result is:

$$\boxed{\vec{M} = g\mu_B \frac{\vec{S}}{\hbar}}, \tag{9.47}$$

where g is the Landé factor which has for electrons in vacuum the numerical value

$$g \approx 2. \tag{9.48}$$

Due to vacuum fluctuations corrections must be taken into account, such that:

$$g = 2 \cdot (1.001159652140(\pm 28)) \quad \text{theory} \tag{9.49}$$

$$= 2 \cdot (1.0011596521884(\pm 43)) \quad \text{experiment} \tag{9.50}$$

The measurement of the g-factor is used as a precision test on quantum field theory.

9.2.1 Normal Zeeman effect

The spectrum of atoms in a magnetic field $\vec{B}$ is measured by optical spectroscopy.

- For $\vec{B} = 0$ the $(2l+1)$ states $|l, l\rangle$, $|l, l-1\rangle$, $\ldots$, $|l, -l\rangle$ are degenerate.
- If we choose the z-axis parallel to the magnetic field $\vec{B}$, we get for $\vec{B} \neq 0$

$$\begin{aligned} & \left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{\hbar^2 l(l+1)}{2mr^2} - \mu_B m B \right] \psi_{nlm}(\vec{r}) \\ = \; & E_{nm} \psi_{nlm} m, \end{aligned} \tag{9.51}$$

where m is the magnetic quantum number and $\mu_B m B$ is equal to $\mu_B B L_z/\hbar$. The $(2l+1)$ states split in a magnetic field with

$$\boxed{\Delta E_m(B) = -\mu_B m B}\,, \tag{9.52}$$

and

$$m = l, \ldots, -l. \tag{9.53}$$

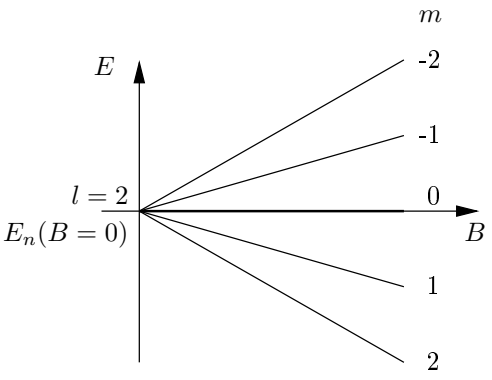

Figure 9.1: Splitting of atomic spectral lines into equidistant „multiplets“

Analogous splitting of spin states

$$\boxed{\Delta E_m(B) = -g \mu_B m B}\,, \tag{9.54}$$

with $m = \pm 1/2$.

Chapter 10

Addition of Angular Momenta

Now we want to treat the problem of adding several angular momenta to one total angular momentum.

- A particle may have orbital angular momentum and spin, e.g.

$$\begin{pmatrix} \psi_\uparrow(\vec{r}) \\ \psi_\downarrow(\vec{r}) \end{pmatrix}. \tag{10.1}$$

- Two or more particles with angular momentum and/or spin, e.g.

$$\psi(\vec{r}_1)\,\psi(\vec{r}_2). \tag{10.2}$$

Each angular momentum l_i- or spin s_i-degree of freedom corresponds to its own $(2l_i+1)$ or $(2s_i+1)$ - dimensional Hilbert space. We consider only the case of 2 angular momenta j_1, j_2, where each one can be either orbital angular momentum, l, or spin, s.

The total Hilbert space is the direct product space of the Hilbert spaces for each j_1, j_2,

$$H = H_{j_1} \otimes H_{j_2}. \tag{10.3}$$

A basis set of H are the $(2j_1+1)\,(2j_2+1)$ - dimensional product states, product basis, with $m_1 = j_1, .., -j_1, \quad m_2 = j_2, .., -j_2$,

$$|\, j_1\, m_1\rangle \otimes |\, j_2\, m_2\rangle = |\, j_1\, m_1, j_2\, m_2\rangle \tag{10.4}$$

$$\vec{J}_i^{\,2}\,|\, j_1\, m_1, j_2\, m_2\rangle = \hbar^2 j_i\,(j_i+1)\,|\, j_1\, m_1, j_2\, m_2\rangle \tag{10.5}$$

$$(J_i)_z\,|\, j_1\, m_1, j_2\, m_2\rangle = \hbar\, m_i\,|j_1\, m_1, j_2\, m_2\rangle \tag{10.6}$$

The total angular momentum operator is the sum of the individual angular momentum operators due to the correspondence principle,

$$\vec{J} = \vec{J}_1 \otimes \mathbb{1} + \mathbb{1} \otimes \vec{J}_2. \tag{10.7}$$

This is a sum of direct products of operators where $\vec{J}_1$ is acting on the Hilbert space of angular momentum 1 and where the identity $\mathbb{1}$ is leaving states in the Hilbert space of angular momentum 2 invariant.

In the following we will use the shorthand notation

$$\vec{J} = \vec{J}_1 + \vec{J}_2, \tag{10.8}$$

where the direct product is tacitly understood. We have

$$[J_{kx}, J_{ly}] = i\hbar\, J_{kz}\delta_{kl}, \quad k, l = 1, 2 \tag{10.9}$$

such that

$$[J_x, J_y] = \sum_{k,l=1,2} [J_{kx}, J_{lx}] = i\hbar \sum_{k=1,2} J_{kz} = i\hbar J_z \tag{10.10}$$

$$[J_z, J_x] = i\hbar J_y \tag{10.11}$$

$$[J_y, J_z] = i\hbar J_x. \tag{10.12}$$

Problem:
What are the eigenstates of the total angular momentum J^2, J_z?

10.1 Example: Two spins $s_i = \frac{1}{2}$, $(i = 1, 2)$

$$s_i = \frac{1}{2}\,, \quad m_i = \begin{cases} \frac{1}{2} \equiv \uparrow \\ -\frac{1}{2} \equiv \downarrow \end{cases} \tag{10.13}$$

The product basis in the ket-notation reads

$$
\begin{aligned}
|1,\,2\rangle &= |s_1,\,m_1\,;s_2,\,m_2\rangle && (10.14)\\
|\uparrow,\uparrow\rangle &= |\frac{1}{2},\,\frac{1}{2};\,\frac{1}{2},\,\frac{1}{2}\rangle && (10.15)\\
|\uparrow,\downarrow\rangle &= |\frac{1}{2},\,\frac{1}{2};\,\frac{1}{2},\,-\frac{1}{2}\rangle && (10.16)\\
|\downarrow,\uparrow\rangle &= |\frac{1}{2},\,-\frac{1}{2};\,\frac{1}{2},\,\frac{1}{2}\rangle && (10.17)\\
|\downarrow,\downarrow\rangle &= |\frac{1}{2},\,-\frac{1}{2};\,\frac{1}{2},\,-\frac{1}{2}\rangle && (10.18)
\end{aligned}
$$

which becomes in coordinate representation of the product basis

$$
\begin{aligned}
|\uparrow,\uparrow\rangle &= \begin{pmatrix} 1\\0\\0\\0 \end{pmatrix} && (10.19)\\
|\uparrow,\downarrow\rangle &= \begin{pmatrix} 0\\1\\0\\0 \end{pmatrix} && (10.20)\\
|\downarrow,\uparrow\rangle &= \begin{pmatrix} 0\\0\\1\\0 \end{pmatrix} && (10.21)\\
|\downarrow,\downarrow\rangle &= \begin{pmatrix} 0\\0\\0\\1 \end{pmatrix}. && (10.22)
\end{aligned}
$$

What are the eigenstates and eigenvalues of $\vec{S}^2 = (\vec{S}_1 + \vec{S}_2)^2$ and $S_z = S_{1z} + S_{2z}$?

By definition, S_z is diagonal in the product basis so that we get

$$\begin{aligned} S_z|\uparrow\uparrow\rangle &= (S_{1z}+S_{2z})|\uparrow\uparrow\rangle && (10.23)\\ &= \hbar\left(\frac{1}{2}+\frac{1}{2}\right)|\uparrow\uparrow\rangle = \hbar|\uparrow\uparrow\rangle && (10.24)\\ S_z|\uparrow\downarrow\rangle &= \hbar\left(\frac{1}{2}-\frac{1}{2}\right)|\uparrow\downarrow\rangle = 0|\uparrow\downarrow\rangle && (10.25)\\ S_z|\downarrow\uparrow\rangle &= 0|\downarrow\uparrow\rangle && (10.26)\\ S_z|\downarrow\downarrow\rangle &= -\hbar|\downarrow\downarrow\rangle. && (10.27) \end{aligned}$$

In coordinate representation (product basis) we then get

$$S_z \to \hbar \begin{array}{c} \begin{matrix} \uparrow\uparrow & \uparrow\downarrow & \downarrow\uparrow & \downarrow\downarrow \end{matrix} \\ \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \end{array}, \tag{10.28}$$

which is obviously diagonal. The eigenvalue $S_z = 0$ is twofold degenerate, since it is realized by the configurations $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$. Since

$$\vec{S}^2 = (\vec{S}_1+\vec{S}_2)^2 = \vec{S}_1^2+\vec{S}_2^2+2\,\vec{S}_1\cdot\vec{S}_2 \tag{10.29}$$

and

$$\begin{aligned} \left[\vec{S}^2, \vec{S}_i^2\right] &= 0 \qquad i=1,2 && (10.30)\\ \left[\vec{S}^2, S_{iz}\right] &= 2\left[\vec{S}_1\cdot\vec{S}_2,\, S_{iz}\right] \neq 0 \qquad i=1,2 && (10.31) \end{aligned}$$

are valid, we cannot expect that there is a simultaneous eigenbasis of $\vec{S}^2$ and S_{iz} .

In coordinate representation (product basis) we also get

$$\vec{S}^2 \to \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix}, \tag{10.32}$$

which is diagonal, too. The product states $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$ with all m_i equal are eigenstates of $\vec{S}^2$, the "mixed" states $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$ are not.

$\vec{S}^2$ can be diagonalized in the $m = 0$ subspace $\{|\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle\}$ with eigenstates and eigenvalues.

$$\begin{aligned} |\, s = 0,\, m = 0\rangle &= \tfrac{1}{\sqrt{2}}\,(\,|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\,) && (10.33)\\ s\,(s+1) &= 0 \\ |\, s = 1,\, m = 0\rangle &= \tfrac{1}{\sqrt{2}}\,(\,|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\,) && (10.34)\\ s\,(s+1) &= 2 \end{aligned}$$

The arbitrary phase prefactor is by convention chosen to be 1. Hence, we have the 4 states with well-defined total s, m.

$$\begin{aligned} |\,0\,0\rangle &= \frac{1}{\sqrt{2}}\,(\,|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\,) && (10.35)\\ |1\,1\rangle &= |\uparrow\uparrow\rangle && (10.36)\\ |\,1\,0\rangle &= \frac{1}{\sqrt{2}}\,(\,|\downarrow\uparrow\rangle + |\downarrow\uparrow\rangle\,) && (10.37)\\ |\,1\,-1\rangle &= |\downarrow\downarrow\rangle, && (10.38) \end{aligned}$$

where the state with $s = 0, m = 0$ is a singlet and the states $s = 1, m = 0, \pm 1$ form a triplet. The product space is therefore decomposed into subspaces with well-defined s, i.e.

$$\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0. \tag{10.39}$$

The 1 represents a triplet and the 0 represents a singlet.

- Checking the degeneracy yields

$$2 \cdot 2 = 3 + 1. \tag{10.40}$$

- Analysing the symmetries results in an antisymmetric singlet and a symmetric triplet. ($\rightarrow$ Pauli's principle, He atom ground state)

- Which basis to choose?
  For

$$H = -g\,\frac{q}{2mc}\,\vec{B}\,(\vec{S}^{(1)} + \vec{S}^{(2)}) \tag{10.41}$$

one can see that

$$S_z^{(1)}, S_z^{(2)} \tag{10.42}$$

is a good choice and for

$$H = \lambda \vec{S}^{(1)} \vec{S}^{(2)} = \frac{\lambda}{2} \left(\vec{S}^2 - \vec{S}^{(1)^2} - \vec{S}^{(2)^2} \right) \tag{10.43}$$

one should choose the basis

$$\vec{S}, S_z. \tag{10.44}$$

10.2 Generalization of 10.1

- J_z diagonal in the product basis
- The naiv method is to diagonalize $\vec{J}^2$, but a better method is to use the raising and lowering operators.
- **Possible values of j**
  The maximum values of j are given by

$$j_{\max} = j_1 + j_2 \tag{10.45}$$

and

$$j_{\min} = |j_1 - j_2|. \tag{10.46}$$

Checking the degeneracy here gives

$$\begin{aligned} \sum_{j=j_1-j_2}^{j_1+j_2} (2j+1) &= \sum_{k=0}^{2j_2} 2\left(j_1 - j_2 + k\right) + 1 && (10.47) \\ &= \left(2\left(j_1 - j_2\right) + 1\right)\left(2j_2 + 1\right) \\ &\quad + 2j_2\left(2j_2 + 1\right) && (10.48) \\ &= \left(2j_1 + 1\right)\left(2j_2 + 1\right). && (10.49) \end{aligned}$$

Example: $\frac{1}{2} \otimes \frac{1}{2}$
At first we consider the case $s = 1$.

$$|\,1\,1\rangle = |\uparrow\uparrow\rangle \tag{10.50}$$

This state is by phase convention properly normalized (Gordon-Shortley). On the one hand we have

$$S_-|\,1\,1\rangle = \sqrt{2}\hbar\,|\,1\,0\rangle \tag{10.51}$$

and on the other hand

$$(S_-^{(1)} + S_-^{(2)})\,|\uparrow\uparrow\rangle = \hbar\,(\,|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle\,) \tag{10.52}$$

so that we get

$$|\,1\,0\rangle = \frac{1}{\sqrt{2}}\,(\,|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\,). \tag{10.53}$$

The state $|\,1,\,-1\rangle = |\downarrow\downarrow\rangle$ is obvious, but can also be calculated as follows,

$$\begin{aligned} S_-|\,1\,0\rangle &= \hbar\sqrt{2}\,|\,1-1\rangle & (10.54)\\ (S_-^{(1)} + S_-^{(2)})\,\frac{1}{\sqrt{2}}\,(\,|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\,) &= \sqrt{2}\hbar\,|\downarrow\downarrow\rangle, & (10.55) \end{aligned}$$

i.e.

$$|\,1,\,-1\rangle = |\downarrow\downarrow\rangle. \tag{10.56}$$

Now we consider the case $s = 0$. The state $|\,0\,0\rangle$ has to be a linear combination of all states which fulfill $m = 0$, i.e. here

$$|\,0\,0\rangle = A|\uparrow\downarrow\rangle + B\,|\downarrow\uparrow\rangle, \tag{10.57}$$

which indeed has $m = 0$. The normalization finally yields

$$\frac{1}{\sqrt{2}}\,(\,|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\,). \tag{10.58}$$

Checking that there is really no other possible state gets us

$$S_\pm|\,0\,0\rangle = 0, \tag{10.59}$$

like expected.

We can formulate this procedure in a more general form. The maximal state is given by

$$|\,j_1 + j_2,\,j_1 + j_2\rangle = |\,j_1\,j_1\rangle \otimes |\,j_2\,j_2\rangle. \tag{10.60}$$

From here on all states with $j = j_1 + j_2$ can be generated by the action of J_-. The orthonormality condition gives us

$$|\,j_1 + j_2 - 1,\,j_1 + j_2 - 1\rangle \perp |\,j_1 + j_2,\,j_1 + j_2 - 1\rangle, \tag{10.61}$$

i.e. that only two terms can appear in linear combinations.

10.3 Clebsch-Gordon Coefficients

It is desired to construct from the basis

$$|j_1\, m_1\, j_2\, m_2\rangle = |j_1\, m_1\rangle\, |j_2\, m_2\rangle \tag{10.62}$$

the eigenvectors of $J_z, \vec{J}^2$ which form a new basis. What we want to do is nothing else but a change of the basis. Since $\vec{J}_1^2$ and $\vec{J}_2^2$ commute with every component of $\vec{J}$, we, hence, obtain

$$\left[J_z, \vec{J}_1^2\right] = \left[J_z, \vec{J}_2^2\right] = \left[\vec{J}^2, \vec{J}_1^2\right] = \left[\vec{J}^2, \vec{J}_2^2\right] = 0. \tag{10.63}$$

The eigenvectors of J_z and $\vec{J}^2$ can be required to be simultaneously eigenvectors of $\vec{J}_1^2$ and $\vec{J}_1^2$ also. At this point it is to stress that $\vec{J}^2$ does **not** commute with J_{1z} or J_{2z}! In the subspace of the simultaneous eigenvectors of $\vec{J}_1^2$ and $\vec{J}_2^2$ with eigenvalues j_1 and j_2 respectively we can write the transformation equation

$$|\, j\, m, j_1\, j_2\rangle = \sum_{m_1 m_2} |\, j_1\, m_1\, j_2\, m_2\rangle\langle j_1\, m_1\, j_2\, m_2|\, j\, m\, j_1\, j_2\rangle, \tag{10.64}$$

which connects the two sets of normalized eigenvectors. The problem of adding angular momenta is thus the problem of determining the transformation coefficients

$$\langle j_1\, m_1\, j_2\, m_2|\, j\, m\, j_1\, j_2\rangle. \tag{10.65}$$

These elements of the transformation matrix are called *vector addition* or *Clebsch-Gordon* or *Wigner coefficients*.

Now we apply the operator $J_z = J_{1z} + J_{2z}$ to (10.64) and get

$$J_z\, |\, j\, m, j_1\, j_2\rangle = m\hbar |\, j\, m, j_1\, j_2\rangle, \tag{10.66}$$

and

$$(J_{1z} + J_{2z})\ |\, j\, m, j_1\, j_2\rangle = (m_1 + m_2)\hbar\, |\, j\, m, j_1\, j_2\rangle. \tag{10.67}$$

By this we can conclude the condition

$$m = m_1 + m_2, \tag{10.68}$$

because otherwise the Clebsch-Gordon coefficients vanish. Doing the same with the operators J_+ and J_- yields after some lengthy calculations the condition

$$|j_1 - j_2| \leq j \leq j_1 + j_2. \tag{10.69}$$

One of the most useful symmetry relations for the Clebsch-Gordon coefficients reads

$$\begin{aligned} & \langle j_1\, m_1\, j_2\, m_2 |\, j\, m\, j_1\, j_2 \rangle & (10.70)\\ = \;& (-1)^{j-j_1-j_2} \langle j_2\, m_2\, j_1\, m_1 |\, j\, m\, j_2\, j_1 \rangle & (10.71)\\ = \;& \langle j_2\, -m_2\, j_1\, -m_1 |\, j\, -m\, j_2\, j_1 \rangle. & (10.72) \end{aligned}$$

Another useful relation for the transition from $j_2\, m_2\, j\, m$ to j, $-m$, j_2, $-m_2$ is given by

$$(-1)^{j_1-m_1} \sqrt{\frac{2j+1}{2j_2+1}}. \tag{10.73}$$

Since the Clebsch-Gordon coefficients are real, the transformation matrix is orthogonal. Furthermore $m_1 = j_1$ is positive by phase convention.

The closed formula finally reads

$$\begin{aligned} & \langle j_1\, m_1\, j_2\, m_2 | j\, m\, j_1\, j_2 \rangle & (10.74)\\ = \;& \sqrt{\tfrac{(2j+1)\,(j_1+j_2-j)!\,(j_1-m_1)!\,(j_2-m_2)!\,(j+m)!}{(j_1+j_2+1)!\,(j_1-j_2+j)!\,(j_2-j_1+j)!\,(j_1+m_1)!\,(j_2+m_2)!\,(j-m)!}} \\ & \times \delta_{m,\, m_1+m_2} \sum_{n=0}^{j-m} (-1)^{j_1-m_1-n} \binom{j-m}{n} \\ & \times \tfrac{(j_1+m_1+n)!\,(j_2+j-m_1-n)!}{(j_1-m_1-n)!\,(j_2-j+m_1+n)!}. & (10.75) \end{aligned}$$

This becomes in particular,

$$\langle j_1\, j_2\, j_2\, j-j_1 |\, j\, j \rangle = \sqrt{\tfrac{(2j_1)!\,(2j+1)!}{(j_1+j_2+j+1)!\,(j_1-j_2+j)!}}. \tag{10.76}$$

Chapter 11

Time-Independent Perturbation Theory

Most Hamiltonian problems are not exactly solvable, because the potential is too complicated. This and the following two chapters are devoted to approximate solution methods.

- **Perturbation theory**
  Problems where there is a small term, a perturbation, in the Hamiltonian, such that without this term the problem is exactly solvable. The theory provides an approximate solution in the form of a systematic (Taylor) expansion in powers of a small parameter.

- **Time-independent perturbation theory**
  In this case the perturbation is time-independent. The theory provides a power expansion of the eigenstates and eigenenergies of the complete Hamiltonian.

- **Time-dependent perturbation theory**
  Here, the perturbation is explicitly time-dependent. In this case, stationary eigenstates of the complete Hamiltonian do not exist. The theory provides an expansion of the time-dependent eigenstates in terms of the (stationary) eigenstates of the unperturbed Hamiltonian. Thus, it describes how a time-dependent perturbation can induce transitions between the stationary

states of the unperturbed Hamiltonian. Further developments of this theory allow also to describe particle-particle interactions, since one moving, e.g. charged, particle provides a time-dependent potential for the other particle.

- **Non-perturbative methods**
  Variational methods and theories, WKB approximation

11.1 Time-independent perturbation theory: Formalism non-degenerate Perturbation theory

The total Hamiltonian now includes a perturbation operator, i.e.

$$H = H^0 + \lambda V, \tag{11.1}$$

where H^0 is the unperturbed Hamiltonian with orthonormal eigenstate basis $\{|n^0\rangle|\ n = 1, 2, ...\}$, which is assumed to be known, and λV is the perturbation, which is supposed to be "small" in a sense to be specified later. For the parameter λ we claim

$$\lambda \in \mathbb{R}, \quad \lambda \ll 1, \tag{11.2}$$

e.g. the potential strength in units of some characteristic energy. λ is the formal small parameter of the expansion.

The exact eigenstates and eigenenergies of H , expressed in a *perturbation series*, i.e. power series in λ, read

$$|n\rangle = |n^0\rangle + |n^1\rangle + |n^2\rangle + ... \tag{11.3}$$

$$E_n = E_n^0 + E_n^1 + E_n^2 + ..., \tag{11.4}$$

where

$$|n^k\rangle \sim \lambda^k, \quad E_n^k \sim \lambda^k. \tag{11.5}$$

The $|n^k\rangle$, E_n^k are determined by comparing the coefficients of the expansion in each order λ^k.

1st order: Keep terms up to $O(\lambda^1)$

$$\begin{aligned}(H^0+\lambda V)\,[\,|n^0\rangle+|n^1\rangle+O(\lambda^2)\,] &= (E_n^0+E_n^1+O(\lambda^2))\,[\,|n^0\rangle+|n^1\rangle+O(\lambda^2)\,]\\ H^0\,|n^1\rangle+\lambda V\,|n^0\rangle &= E_n^0\,|n^1\rangle+E_n^1\,|n^0\rangle+O(\lambda^2),\end{aligned}$$

because $O(\lambda^0)$ fulfills

$$H^0\,|n^0\rangle = E_n^0\,|n^0\rangle. \tag{11.6}$$

a) **Correction to the eigenenergy**
Since $|n^0\rangle$ is normalized, i.e.

$$\langle n^0|n^0\rangle = 1, \tag{11.7}$$

we get by multiplying equation (11.6) by $\langle n^0|$

$$\langle n^0|H^0|n^1\rangle = E_n^0\langle n^0|n^1\rangle \tag{11.8}$$

and

$$\boxed{E_n^1 = \langle n^0|\lambda V|n^0\rangle}\,. \tag{11.9}$$

This is a first order correction to the energy eigenvalue. This correction is, as demanded, linear in λ and it involves only eigenstates of the unperturbed Hamiltonian.

b) **Correction to the eigenstate:**
We make an expansion in $\{|n\rangle\}$ as follows,

$$|n^1\rangle = \sum_m |m^0\rangle\langle m^0|n^1\rangle. \tag{11.10}$$

Assuming

$$E_m^0 \neq E_n^0, \quad \forall m \neq n, \tag{11.11}$$

i.e. we apply a non-degenerate perturbation theory, we get by multiplying equation (11.6) by $\langle m^0|$

$$\langle m^0|H^0|n^1\rangle + \langle m^0|\lambda V|n^0\rangle = \langle m^0|E_n^0|n^1\rangle \tag{11.12}$$

$$\Leftrightarrow E_m^0\langle m^0|n^1\rangle + \langle m^0|\lambda V|n^0\rangle = E_n^0\langle m^0|n^1\rangle. \tag{11.13}$$

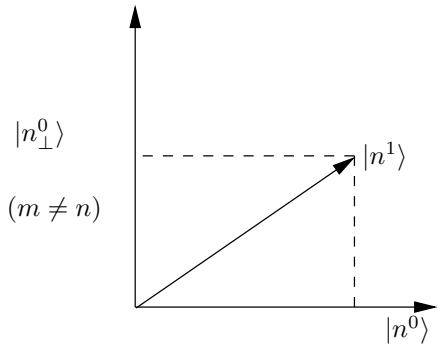

Figure 11.1: Vector representation of the eigenstate

The expansion coefficients for $m \neq n$ therefore are

$$\langle m^0|n^1\rangle = \frac{\langle m^0|\lambda V|n^0\rangle}{E_n^0 - E_m^0}. \tag{11.14}$$

The expansion coefficient for $m = n$ and $a_n = \langle n^0|n^1\rangle$ is determined by the normalization of the total eigenstate, up to order $O(\lambda^1)$.

$$\begin{aligned}
|n\rangle &= |n^0\rangle + |n^1\rangle + O(\lambda^2) && (11.15)\\
&= (1+a_n)|n^0\rangle + \sum_{m\neq n} |m^0\rangle \tfrac{\langle m^0|\lambda V|n^0\rangle}{E_n^0 - E_m^0} && (11.16)\\
\langle n|n\rangle &= |1+a_n|^2 + \sum_{m\neq n} \tfrac{|\langle m^0|\lambda V|n^0\rangle|^2}{(E_n^0 - E_m^0)^2} && (11.17)\\
&= |1+a_n|^2 + O(\lambda^2) && (11.18)\\
&= 1 + |a_n|^2 + a_n + a_n^* && (11.19)\\
&= 1 + O(\lambda^2) + a_n + a_n^* && (11.20)\\
&\stackrel{!}{=} 1 + O(\lambda^2) && (11.21)
\end{aligned}$$

By this we get

$$a_n = i\alpha, \quad \alpha \in \mathbb{R} \tag{11.22}$$

and

$$1 + a_n = e^{i\alpha} + O(\lambda^2). \tag{11.23}$$

The component of $|n^1\rangle$ parallel to the unperturbed $|n^0\rangle$ is only changed by a phase factor in $O(\lambda^1)$. We can therefore multiply $|n^1\rangle$ by an overall phase factor, i.e.

$$\begin{aligned} |n\rangle \longrightarrow |n\rangle\, e^{-i\alpha} &= |n^0\rangle + \sum_{m\neq n} |m^0\rangle \, \tfrac{\langle m^0|\lambda V|n^0\rangle}{E_n^0 - E_m^0} \\ &\quad \times(1 - i\alpha + O(\lambda^2)) \qquad (11.24) \\ &= |n^0\rangle + \sum_{m\neq n} |m^0\rangle \, \tfrac{\langle m^0|\lambda V|n^0\rangle}{E_n^0 - E_m^0} \\ &\quad \times(1 - O(\lambda) + O(\lambda^2)). \qquad (11.25) \end{aligned}$$

We then get the first order correction to the eigenstates as

$$\boxed{|n\rangle = |n^0\rangle + \sum_{m\neq 0} |m^0\rangle \, \tfrac{\langle m^0|\lambda V|n^0\rangle}{E_n^0 - E_m^0}} \,. \qquad (11.26)$$

This correction involves only eigenstates and energies of the unperturbed Hamiltonian H^0 and up to the order $O(\lambda^1)$ the component of $|n^1\rangle$ parallel to the corresponding unperturbed $|n^0\rangle$ is not changed by the perturbation. Furthermore

$$|n^1\rangle \perp |n^0\rangle \qquad (11.27)$$

is valid.

2nd order:

$$\begin{aligned} & (H^0 + \lambda V)\,[\,|n^0\rangle + |n^1\rangle + |n^2\rangle + O(\lambda^3)\,] \qquad (11.28) \\ = \;& (E_n^0 + E_n^1 + E_n^2)\,[\,|n^0\rangle + |n^1\rangle + |n^2\rangle\,], \qquad (11.29) \end{aligned}$$

which is fulfilled in $O(\lambda^0)$, $O(\lambda^1)$ by construction of E_n^1, $|n^1\rangle$. We only consider terms of second order, i.e. $O(\lambda^2)$.

$$H^0\,|n^2\rangle + \lambda V\,|n^1\rangle = E_n^0\,|n^2\rangle + E_n^1\,|n^1\rangle + E_n^2\,|n^0\rangle \qquad (11.30)$$

By multiplying this equation by $\langle n^0|$ and paying attention to the relation

$$\langle n^0|n^1\rangle = 0, \qquad (11.31)$$

we get

$$\langle n^0|H^0|n^2\rangle = E_n^0\langle n^0|n^2\rangle, \tag{11.32}$$

and by this the 2nd order correction to the energy eigenvalues,

$$\boxed{E_n^2 = \langle n^0|\lambda V|n^1\rangle = \sum_{m\neq n} \frac{|\langle n^0|\lambda V|m^0\rangle|^2}{E_n^0 - E_m^0}}. \tag{11.33}$$

For the ground state, i.e. $n = 0$, we obtain

$$E_0^2 < 0, \tag{11.34}$$

which means that the 2nd order correction to the ground state energy is always < 0.

Discussion of the validity of perturbation theory

The perturbation series gives meaningful results, i.e. it converges, if the terms of the perturbation series decrease in size fast enough as the order (λ^k) increases,

$$\left|\frac{\langle m^0|\lambda V|n^0\rangle}{E_n^0 - E_m^0}\right| \ll 1. \tag{11.35}$$

In general, this is the case for small λ. But it always fails for arbitrary λ , if $E_m^0 \longrightarrow E_n^0$ or $E_m^0 = E_n^0$ for some $m \neq n$.

In this case one must apply degenerate perturbation theory. The formulas for $|n^1\rangle$ and for E_n^2 show that n given states $|m^0\rangle$ contribute the more to the correction to $|n^0\rangle$, the smaller the energy difference between the two states is. If $E_m^0 = E_n^0$, the state is unstable to a perturbation, $|m^0\rangle$ and $|n^0\rangle$ "mix" strongly, not proportional to λ.

11.2 Degenerate perturbation theory

The full Hamiltonian in perturbation theory was given by

$$H = H^0 + \lambda V. \tag{11.36}$$

Now we consider the case that H^0 has a degenerate subspace of eigenstates

$$M = \{|m_1\rangle, ..., |m_k\rangle\}, \tag{11.37}$$

with

$$E^0_{m_1} = E^0_{m_2} = ... = E^0_{m_k} = E^0_m. \tag{11.38}$$

Then, the corrections due to λV cannot be calculated using the method derived in the last section. We have to distinguish between the following cases.

a) λV **is also degenerate in this subspace** M

$$\lambda V |m_i\rangle = v_{m_i} |m_i\rangle \tag{11.39}$$

Then $H = H^0 + \lambda V$ is also diagonal in this subspace,

$$(H^0 + \lambda V) |m_i\rangle = (E^0_{m_i} + v_{m_i}) |m_i\rangle, \tag{11.40}$$

and the problem is already solved in the space M.

b) λV **is non-degenerate in this subspace** M

Example:
Consider $H^0, \lambda V$ in an eigenstate basis representation of H^0.

$$H^0 = \begin{bmatrix} E^0_m & & 0 \\ & E^0_m & \\ 0 & & E^0_m \end{bmatrix} \tag{11.41}$$

$$\lambda V = \lambda \begin{bmatrix} 0 & v_{12} & v_{13} \\ v_{21} & 0 & v_{23} \\ v_{31} & v_{32} & 0 \end{bmatrix} \tag{11.42}$$

Solution:
Diagonalize λV in the degenerate subspace M. Since H^0 is degenerate in M, it remains diagonal by this procedure.

- The diagonalization problem of λV in the degenerate subspace(s) of H^0 is often tractable, since the dimension of the subspace is often low, e.g. $d = 2$.

- By diagonalization of λV in the subspace M, the eigenvalue problem of the complete system $H^0 + \lambda V$ is solved exactly in the degenerate subspace M.
- This basis transformation lifts, in general, the degeneracy of $H^0 + \lambda V$ in the degenerate subspace of H^0. One can then proceed in the new basis, using non-degenerate perturbation theory.
- λV can have matrix elements $\langle n|\lambda V|m_i\rangle$ which connect states in the degenerate subspace M with states outside of M. These matrix elements are not taken into account in the diagonalization of λV within M. They are treated afterwards by regular perturbation theory.

Example: Degenerate perturbation theory
Assume that an eigenstate basis of H^0 is given.

$$H^0 = \begin{bmatrix} E_1^0 & & & 0 \\ & E_2^0 & & \\ & & E_m^0 & \\ 0 & & & E_m^0 \end{bmatrix} \tag{11.43}$$

$$\lambda V = \begin{bmatrix} 0 & v_{12} & v_{13} & v_{14} \\ v_{12}^* & 0 & v_{23} & v_{24} \\ v_{13}^* & v_{23}^* & 0 & v_m \\ v_{14}^* & v_{24}^* & v_m^* & 0 \end{bmatrix}, \tag{11.44}$$

with

$$M = \begin{pmatrix} 0 & v_m \\ v_m^* & 0 \end{pmatrix}, \tag{11.45}$$

i.e. only rotations in the subspace M.

1. Diagonalize $H^0 + \lambda V$ in M.

$$\begin{pmatrix} E_m^0 - E & v_m \\ v_m^* & E_m^0 - E \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0 \tag{11.46}$$

$$(E_m^0 - E)^2 - |v_m|^2 = 0 \tag{11.47}$$

$$\Leftrightarrow E_m^0 \pm |v_m| = E_{1,2}, \tag{11.48}$$

with corresponding new eigenvectors $|\widetilde{m}_1\rangle$, $|\widetilde{m}_2\rangle$.

2. Redefine $H^0, \lambda V$ in the new eigenstate basis.

$$\widetilde{H}^0 = \begin{bmatrix} E_1^0 & & & 0 \\ & E_2^0 & & \\ & & E_m^0 - |v_m| & \\ 0 & & & E_m^0 + |v_m| \end{bmatrix} \tag{11.49}$$

$$\lambda\widetilde{V} = \begin{bmatrix} 0 & v_{12} & v_{13} & v_{14} \\ v_{12}^* & 0 & v_{23} & v_{24} \\ v_{13}^* & v_{23}^* & 0 & 0 \\ v_{14}^* & v_{24}^* & 0 & 0 \end{bmatrix} \tag{11.50}$$

   The perturbation is removed in M.

3. Proceed with $\widetilde{H}^0, \lambda\widetilde{V}$ using non-degenerate perturbation theory.

11.3 Example: Stark effect

Consider a charged particle with charge q in a binding potential, subjected to an externally applied, homogenous electric field

$$E = -\frac{\partial\phi}{\partial x}. \tag{11.51}$$

Here, the binding potential is the one of the harmonic oscillator (see figure 11.2), so that we get the full Hamiltonian

$$H = H^0 + V^0 - \lambda V \tag{11.52}$$

$$= \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - qEx. \tag{11.53}$$

The perturbation operator x in an eigenstate basis of H^0 reads

$$x = \sqrt{\tfrac{\hbar}{2m\omega}}(a + a^\dagger). \tag{11.54}$$

Hence, we get by this

$$H = \hbar\omega(a^\dagger a + \tfrac{1}{2}) - qE\sqrt{\tfrac{\hbar}{2m\omega}}(a + a^\dagger). \tag{11.55}$$

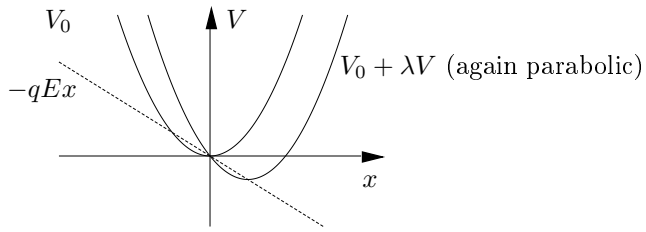

Figure 11.2: Binding potential of the harmonic oscillator

The shifted potential is given by

$$\frac{1}{2}m\omega^2 x^2 - qEx = \frac{1}{2}m\omega^2 \left(x - \frac{qE}{m\omega^2}\right)^2 - \frac{(qE)^2}{2m\omega^2}, \tag{11.56}$$

where the term $(x - qE/2m\omega^2)^2$ is the shifted harmonic oscillator and the term $-(qE)^2/2m\omega^2$ represents a constant downward shift of the energy.

The energy eigenvalue correction of first order perturbation theory yields

$$E_n^1 = \langle n^0 | qE\sqrt{\tfrac{\hbar}{2m\omega}}(a + a^\dagger)|n^0\rangle = 0, \tag{11.57}$$

and in x representation

$$E_n^1 = \int dx\, |\psi_n^0(x)|^2\, qEx = 0, \tag{11.58}$$

since $|\psi_n^0(x)|^2$ is symmetric and qEx is antisymmetric. The calculation of the second order correction reads

$$\begin{aligned}
E_n^2 &= \sum_{m\neq n} \tfrac{|\langle m^0|\, qE\sqrt{\frac{\hbar}{2m\omega}}(a+a^\dagger)\,|n^0\rangle|^2}{E_n^0 - E_m^0} && (11.59)\\
&= (qE)^2 \left(\sqrt{\tfrac{\hbar}{2m\omega}}\right)^2 \left[\tfrac{|\langle n^0+1|\, a^\dagger\,|n^0\rangle|^2}{E_n^0 - E_{n+1}^0} + \tfrac{|\langle n^0-1|\, a\,|n^0\rangle|^2}{E_n^0 - E_{n-1}^0}\right] && (11.60)\\
&= (qE)^2 \frac{\hbar}{2m\omega}\left[\tfrac{|\langle n^0+1|\, a^\dagger\,|n^0\rangle|^2}{-\hbar\omega} + \tfrac{|\langle n^0-1|\, a\,|n^0\rangle|^2}{\hbar\omega}\right] && (11.61)\\
&= (qE)^2 \tfrac{\hbar}{2m\omega}\left[-\tfrac{n+1}{\hbar\omega} + \tfrac{n}{\hbar\omega}\right] && (11.62)\\
&= -\tfrac{(qE)^2}{2m\omega^2} && (11.63)\\
&< 0, && (11.64)
\end{aligned}$$

which is also clear from the sketch of the potential.

Selection rule:
The linear potential $-qEx$ connects only states $n \pm 1$ with n.

The first order correction to the eigenstates can be derived as

$$|n\rangle = |n^0\rangle + \sum_{m \neq n} |m^0\rangle \frac{\langle m^0| -qE\sqrt{\frac{\hbar}{2m\omega}}(a+a^\dagger)|n^0\rangle}{E_n^0 - E_m^0} \tag{11.65}$$

$$= |n\rangle - \frac{qE}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n}\,|(n-1)^0\rangle - \sqrt{n+1}\,|(n+1)\rangle\right) \tag{11.66}$$

Remark:
For a finite binding potential, e.g. $V(r) = \frac{e^2}{r}$, as in figure 11.3, the particle may be ionized from the potential.

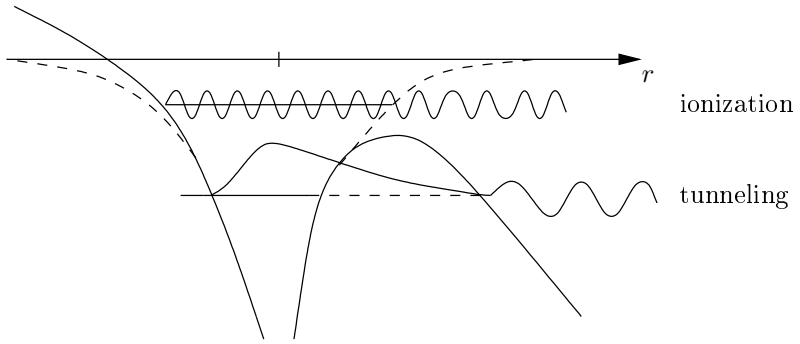

Figure 11.3: Binding potential

11.4 Example: Fine structure of atomic spectra

There are relativistic corrections to the kinetic energy in the hydrogen atom. These will be treated systematically in the course of Quantum Mechanics II. The relativistic treatment implies,

(1) the existence of spin,

(2) the coupling of the spin of a particle to its angular momentum,

(3) and terms proportional to $p^4, p^6 ...$ in the kinetic energy,

$$E_{kin} = \sqrt{m^2c^4 + p^2c^2} - mc^2 = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + ... \tag{11.67}$$

The relativistic corrections are suppressed by a factor

$$\frac{p^2}{4m^2c^2} \ll 1 \tag{11.68}$$

for the hydrogen atom, which we will here not consider. Nevertheless it does play a significant role in heavy atoms, where the inner shells are tightly localized near the nucleus, because of its big charge Ze, so that the average $\langle p^2 \rangle$ becomes relativistically large.

We will now consider the

Spin-Orbit coupling:

Visualization:
In the rest frame of an electron bound to a hydrogen nucleus, the nucleus moves, classically speaking, in a circle around the electron (figure 11.4), and generates a magnetic field,

$$\vec{B} = -\frac{e}{c}\frac{\vec{v} \times \vec{r}}{r^3} = \frac{e\vec{L}}{mcr^3}, \tag{11.69}$$

with e being the proton charge, which is positive, and $\vec{v}$ the velocity of electron which is equal to the proton's velocity, but with opposite sign.

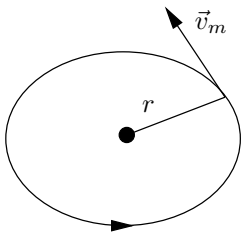

Figure 11.4: Spin-orbit visualization

The electron spin has a magnetic dipole energy in this B-field,

$$\widetilde{H}_{\text{spin-orbit}} = -\frac{e}{mc}\frac{\vec{\mu}\vec{L}}{r^3} \tag{11.70}$$

$$= \frac{e^2}{m^2c^2}\frac{1}{r^3}\,\vec{S}\cdot\vec{L}, \tag{11.71}$$

with

$$\vec{\mu} = g\frac{-e}{2mc}\,\vec{S}, \quad g \approx 2. \tag{11.72}$$

The relativistic treatment gives the correct result,

$$\boxed{H_{\text{spin-orbit}} = \frac{1}{2}\frac{e^2}{m^2c^2}\frac{1}{r^3}\vec{S}\cdot\vec{L}}\,, \tag{11.73}$$

where the prefactor $1/2$ is the so-called *Thomas factor.*

Corrections to the energy eigenvalues due to $H_{s.o.}$
One can write $\vec{S}\cdot\vec{L}$ in terms of the total angular momentum,

$$\vec{S}\cdot\vec{L} = \frac{1}{2}\,(\vec{J}^2 - \vec{L}^2 - \vec{S}^2), \tag{11.74}$$

with

$$\vec{J}^2 = (\vec{L}+\vec{S})^2. \tag{11.75}$$

In the basis of the total angular momentum eigenstates one gets

$$\langle j'm';\, l', \frac{1}{2}|\, H_{\text{spin-orbit}}\,|jm;\, l, \frac{1}{2}\rangle \tag{11.76}$$

$$= \delta_{jj'}\delta_{mm'}\delta_{ll'}\frac{e^2}{4m^2c^2}\,\hbar^2\,[\,j(j+1) - l(l+1) - \tfrac{3}{4}\,] \times \left\langle \frac{1}{r^3}\right\rangle_{nl}, \tag{11.77}$$

With $j = l \pm \frac{1}{2}$ one furthermore gets

$$E^1_{\text{spin-orbit},nl} = \frac{\hbar^2e^2}{4m^2c^2}\left\langle\frac{1}{r^3}\right\rangle_{nl}\begin{cases} l, & j = l+\frac{1}{2} \\ -(l+1), & j = l-\frac{1}{2}\end{cases}\,, \tag{11.78}$$

with

$$\left\langle \frac{1}{r^3} \right\rangle_{nl} = \frac{1}{a_0^3} \frac{1}{n^3 l(l+\frac{1}{2})(l+1)}. \tag{11.79}$$

Therefore the first order energy eigenvalue correction reads

$$\boxed{E^1_{s.o.,nl} = \frac{1}{4} mc^2 \left(\frac{e^2}{\hbar c}\right) \frac{\left\{ \begin{smallmatrix} l \\ -(l+1) \end{smallmatrix} \right\}}{n^3 l(l+\frac{1}{2})(l+1)}}, \tag{11.80}$$

which is valid for $l = 0, 1, 2, ...$ The factor

$$\frac{e^2}{\hbar c} \approx \frac{1}{137} \tag{11.81}$$

is called *fine structure constant.* The heart of the matter is that the spin-orbit splitting lifts the l-degeneracy of the hydrogen spectrum.

Chapter 12

Time-Dependent Perturbation Theory

We now consider time-dependent problems, where the Hamiltonian can be decomposed into a time-independent part H^0, whose eigenstates and eigenenergies are assumed to be known, and a *time-dependent perturbation* $V(t)$,

$$H = H^0 + V(t). \tag{12.1}$$

This leads us to the question of how to describe time-dependence in quantum mechanics in general.

12.1 Representations of time-dependence in quantum mechanics

12.1.1 Schrödinger picture

Any physical property of a system in a state $|\psi\rangle$ is described by the expectation value of the appropriate operator Ω,

$$\langle\Omega(t)\rangle = \langle\psi|\Omega|\psi\rangle, \tag{12.2}$$

which can be time-dependent.

Schrödinger picture
Let Ω_s be a time-independent operator, except for possible explicit t-dependence, and let $|\psi_s\rangle = |\psi_s(t)\rangle$ be a time-dependent state. The equation of motion for $|\psi(t)\rangle$ then reads

$$i\hbar\frac{d}{dt}|\psi_s(t)\rangle = H|\psi_s(t)\rangle. \tag{12.3}$$

The time evolution of $|\psi(t)\rangle$ is formally described by the time evolution operator $U(t, t_0)$,

$$|\psi_s(t)\rangle = U(t, t_0)|\psi(t_0)\rangle, \tag{12.4}$$

with the initial condition $|\psi(t_0)\rangle$. In chapter 5 we had given a procedure of how to calculate U in x-representation by path integrals. This will not be considered here.

Example: H time independent
Then

$$|\psi_s(t)\rangle = e^{-\frac{i}{\hbar}Ht}|\psi(t_0)\rangle \tag{12.5}$$

is a formal solution of the Schrödinger equation

$$i\hbar\tfrac{d}{dt}|\psi_s(t)\rangle = H|\psi_s(t)\rangle, \tag{12.6}$$

with

$$U(t, t_0) = e^{-\frac{i}{\hbar}Ht}. \tag{12.7}$$

If $H = H^0 + V(t)$ is time-dependent, then $U(t, t_0)$ cannot be written in the simple exponential form, since the t-dependence of H would give an additional term in $\frac{d}{dt}|\psi(t)\rangle$.

It is our goal to develop an efficient, perturbative method for calculating $U(t, t_0)$ and, hence, $|\psi_s(t)\rangle$ for such time dependent problems.

General properties of $U(t, t_0)$

1. The time evolution operator $U(t, t_0)$ is unitary, i.e.

$$U^\dagger U = \mathbb{1}, \tag{12.8}$$

since

$$\langle \psi_s(t) \,|\, \psi_s(t) \rangle = 1, \quad \forall t. \tag{12.9}$$

2. $U(t, t_1)\, U(t_1, t_0) = U(t, t_0)$
3. $U(t, t) = \mathbb{1}$
4. $U^\dagger(t_1, t_2) = U(t_2, t_1)$

12.1.2 Heisenberg picture

All the time dependence can be cast from $|\psi(t)\rangle$ into a time dependence of Ω , while keeping all physical predictions of the theory, i.e. $\langle \Omega \rangle(t)$, unchanged.

$$\begin{aligned} \langle \Omega \rangle(t) &= \langle \psi_s(t)| \, \Omega_s \, |\psi_s(t)\rangle & (12.10)\\ &= \langle \psi_s(t_0)| \, U_s^\dagger(t, t_0) \Omega_s U_s(t, t_0) \, |\psi_s(t_0)\rangle & (12.11)\\ &= \langle \psi_H(t)| \, \Omega_H(t) \, |\psi_H(t)\rangle & (12.12) \end{aligned}$$

While Equation (12.10) represents the Schrödinger picture, equation (12.12) represents the Heisenberg picture, in which we have the t-independent state

$$|\psi_H\rangle = |\psi_s(t_0)\rangle, \tag{12.13}$$

and

$$\Omega_H(t) = U_s^\dagger(t, t_0) \Omega_s U_s(t, t_0), \tag{12.14}$$

which is also valid for $\Omega = H$.

Equations of motion for $\Omega_H(t)$ and $U_s(t, t_0)$

$$\begin{aligned} i\hbar \tfrac{d}{dt} \, |\psi_s(t)\rangle &= i\hbar \tfrac{d}{dt} U_s(t, t_0) \, |\psi_s(t_0)\rangle & (12.15)\\ &= H U_s(t, t_0) \, |\psi_s(t_0)\rangle, & (12.16) \end{aligned}$$

which must be fulfilled for all initial conditions $|\psi_s(t_0)\rangle$. Hence, we get

$$i\hbar\frac{d}{dt}U_s(t,t_0) = HU_s(t,t_0), \tag{12.17}$$

and by equation (12.14) moreover

$$i\hbar\frac{d}{dt}\Omega_H(t) = i\hbar\left[\frac{dU_s^\dagger}{dt}\Omega_s U_s + U_s^\dagger\Omega_s\frac{dU_s}{dt} + U_s^\dagger\frac{\partial\Omega_s}{\partial t}U_s\right], \tag{12.18}$$

with

$$-i\hbar\frac{dU_s^\dagger}{dt} = U_s^\dagger H. \tag{12.19}$$

Thus we obtain

$$i\hbar\frac{d}{dt}\Omega_H(t) \;=\; -U_s^\dagger H U_s U_s^\dagger\Omega_s U_s + U_s^\dagger\Omega_s U_s U_s^\dagger H U_s + i\hbar\frac{\partial}{\partial t}\Omega_H(t), \tag{12.20}$$

and finally

$$\boxed{i\hbar\frac{d}{dt}\Omega_H(t) = [\,\Omega_H, H_H\,] + i\hbar\frac{\partial}{\partial t}\Omega_H(t)}\,. \tag{12.21}$$

This equation is in complete analogy to the classical Hamiltonian equation of motion, i.e.

$$\frac{d}{dt}\Omega \;=\; \{\,\Omega, H\,\} + \frac{\partial}{\partial t}\Omega \tag{12.22}$$

$$\{\,\Omega, H\,\} \;=\; \frac{\partial\Omega}{\partial x}\frac{\partial H}{\partial p} - \frac{\partial H}{\partial x}\frac{\partial\Omega}{\partial p} \tag{12.23}$$

Correspondence principle in Heisenberg picture[1]

$$\{\,\Omega, H\,\} \to \frac{1}{i\hbar}[\,\Omega, H\,] \tag{12.24}$$

Remark:
Historically, the Heisenberg picture was first discovered by Heisenberg, when he found from his analysis of atomic spectra that in quantum mechanical physical transition amplitudes have matrix multiplication rules,

$$a_{nm} = \sum_k a_{nk}a_{km}, \tag{12.25}$$

[1] Compare also with the Ehrenfest theorem!

and, hence, must be described as operators. He took the correspondence principle (12.24) as the natural generalization of classical mechanics.
Schrödinger introduced his picture shortly after from a generalized description of interference phenomena. The equivalence was at first not clear, but was shown by Dirac.

Equal-time commutators in Heisenberg picture

$$\begin{aligned}
[\,x_H(t), p_H(t)\,] &= U_s^\dagger(t,t_0) \times U_s(t,t_0) U_s^\dagger(t,t_0)\, p\, U_s(t,t_0) \\
&\quad - U_s^\dagger(t,t_0)\, p\, U_s(t,t_0) U_s^\dagger(t,t_0) \times U_s(t,t_0) && (12.26)\\
&= U_s^\dagger(t,t_0) \times U_s(t,t_0) U_s(t_0,t)\, p\, U_s(t,t_0) \\
&\quad - U_s^\dagger(t,t_0)\, p\, U_s(t,t_0) U_s(t_0,t) \times U_s(t,t_0) && (12.27)\\
&= U_s^\dagger(t,t_0) \times U_s(t,t)\, p\, U_s(t,t_0) \\
&\quad - U_s^\dagger(t,t_0)\, p\, U_s(t,t) \times U_s(t,t_0) && (12.28)\\
&= U_s^\dagger(t,t_0)\, [\,x,p\,]\, U_s(t,t_0) && (12.29)\\
&= i\hbar\, \mathbb{1} && (12.30)
\end{aligned}$$

The commutators for non-equal times are in general more complicated, in particular $\neq 0$, since

$$U(t,t_0)\, U^\dagger(t',t_0) \neq 1. \tag{12.31}$$

12.1.3 Interaction or Dirac picture

For the development of perturbation theory it is useful to separate the "trivial" t-dependence of $|\psi_s(t)\rangle$ due to the stationary time evolution of $\exp\left(-\frac{i}{\hbar}H^0 t\right)$ from the nontrivial t-dependence due to $V(t)$, e.g. for eigenstates of H^0, where the t-development according to H^0 is absorbed in an exponential function, i.e.

$$|n(t)\rangle = e^{-\frac{i}{\hbar}E_t(t-t_0)}\, |n(t_0)\rangle. \tag{12.32}$$

Therefore, we *define* the interaction or Dirac picture as follows.

$$\begin{aligned}
|\psi_I(t)\rangle &= e^{\frac{i}{\hbar}H^0(t-t_0)}\, |\psi_s(t)\rangle = U_s^{0\dagger}(t,t_0)\, |\psi_s(t)\rangle && (12.33)\\
&= U_s^{0\dagger}(t,t_0)\, U_s(t,t_0)\, |\psi_H\rangle && (12.34)
\end{aligned}$$

Equations of motion for $|\psi_I(t)\rangle$ and $\Omega_I(t)$
By

$$-i\hbar\tfrac{d}{dt}U_s^{0\dagger} = U_s^{0\dagger}H_s^0 \tag{12.35}$$

and

$$i\hbar\tfrac{\partial}{\partial t}U_s = [\,H_s^0 + V_s(t)\,]\,U_s \tag{12.36}$$

we get

$$\begin{aligned} & i\hbar\tfrac{d}{dt}\,|\psi_I(t)\rangle \\ = \;& -U_s^{0\dagger}H_s^0U_s\,|\psi_H\rangle + U_s^{0\dagger}(H_s^0+V_s)U_s\,|\psi_H\rangle && (12.37)\\ = \;& U_s^{0\dagger}V_sU_s\,|\psi_H\rangle = U_s^{0\dagger}V_s\,|\psi_s\rangle && (12.38)\\ = \;& U_s^{0\dagger}V_sU_s^0\,|\psi_I(t)\rangle = V_I(t)|\psi_I(t)\rangle \quad . && (12.39)\end{aligned}$$

We then have

$$\begin{aligned} \langle\psi_s(t)|\Omega|\psi_s(t)\rangle &= \langle\psi_I(t)|U_s^{0\dagger}\Omega_sU_s^0|\psi_I(t)\rangle && (12.40)\\ &= \langle\psi_I(t)|\Omega_I(t)|\psi_I(t)\rangle && (12.41)\end{aligned}$$

with

$$\boxed{\begin{aligned} \Omega_I(t) &= U_s^{0\dagger}\Omega_sU_s^0 \\ U_s^0 &= e^{-\frac{i}{\hbar}H^0(t-t_0)} \\ i\hbar\tfrac{\partial}{\partial t}\,|\psi_I(t)\rangle &= V_I(t)\,|\psi_I(t)\rangle \end{aligned}}\;, \tag{12.42}$$

which desribes the time evolution in the interaction picture.

In the interaction picture, the state evolves according to a Schrödinger equation only with the perturbation $V_I(t)$. Any operator evolves like a Heisenberg operator, but with the unperturbed Hamiltonian H^0. The advantage of the interaction picture is that the time evolution of the operators is known.

12.2 Perturbation theory in general

$$|\psi_I(t)\rangle = U_I(t,t_0)\,|\psi_I(t_0)\rangle, \tag{12.43}$$

where U_I is the time evolution operator in the interaction picture. With

$$U_s = U_s^0 U_I \tag{12.44}$$

the equation of motion for U_I reads

$$i\hbar\tfrac{\partial U_I}{\partial t} = V_I U_I. \tag{12.45}$$

Since V_I is t-dependent, we here have no simple exponential solution.

The formal integration with initial condition yields

$$\boxed{U_I(t,t_0) = \mathbb{1} - \tfrac{i}{\hbar}\int_{t_0}^{t} dt'\; V_I(t')U_I(t',t_0)}\;, \tag{12.46}$$

which is known as the *Lippmann-Schwinger integral equation.* The Lippmann-Schwinger equation can be solved by iteration. This generates the desired power series in $V_I(t)$.

$$\begin{aligned} U_I(t,t_0) &= \mathbb{1} - \tfrac{i}{\hbar}\int_{t_0}^{t} dt'\; V_I(t') + (-\tfrac{i}{\hbar})^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; V_I(t')V_I(t'') \\ &\quad + (-\tfrac{i}{\hbar})^3 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} dt'''\; V_I(t')\cdot V_I(t'')V_I(t''') \\ &\quad + \ldots \qquad (12.47) \\ U_s(t,t_0) &= U_s^0(t,t_0)U_I(t,t_0) \qquad (12.48) \end{aligned}$$

It would be convenient to have the upper integral bounds independent of the integration variables.

$$\begin{aligned} \widehat{T}\int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\; V_I(t')V_I(t'') &= \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; V_I(t')V_I(t'') \\ &\quad + \int_{t_0}^{t} dt' \int_{t'}^{t} dt''\; V_I(t'')V_I(t') \qquad (12.49) \\ &= \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; V_I(t')V_I(t'') \\ &\quad + \int_{t_0}^{t} dt'' \int_{t''}^{t} dt'\; V_I(t')V_I(t'') \qquad (12.50) \end{aligned}$$

These integrals share the same integration area, since the integrands in both parts of the integral are equal (see figure 12.1).

We then obtain

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \; V_I(t')V_I(t'') = \tfrac{1}{2}\,\widehat{T} \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \; V_I(t')V_I(t''), \tag{12.51}$$

with

$$\widehat{T}\{\, V_I(t_1)V_I(t_2)\,\} = \begin{cases} V_I(t_1)\, V_I(t_2) & , t_1 > t_2 \\ V_I(t_2)\, V_I(t_1) & , t_1 < t_2 \end{cases} . \tag{12.52}$$

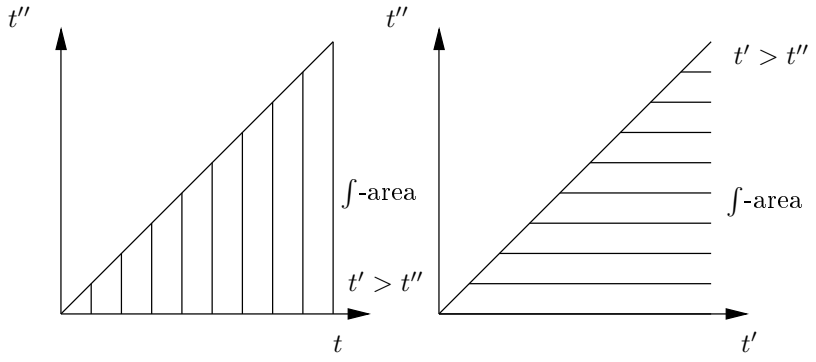

Figure 12.1: Integration area for perturbation V_I

Consequently the time evolution operator reads

$$\boxed{U_I(t,t_0) = \widehat{T} e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' \; V_I(t')}} \tag{12.53}$$

Since $U_I(t,t_0)$ and $|\psi_I(t)\rangle$ have the same equation of motion in terms of t,

$$i\hbar\tfrac{\partial}{\partial t}\,|\psi_I(t)\rangle = V_I(t)\,|\psi_I(t)\rangle = U^{0\dagger} V_s U^0\,|\psi_I(t)\rangle, \tag{12.54}$$

we can write the same perturbation expansion for $|\psi_I(t)\rangle$ as for $U_I(t,t_0)$.

$$\boxed{|\psi_I(t)\rangle = |\psi_I(t_0)\rangle - \tfrac{i}{\hbar}\int_{t_0}^{t} dt' \; V_I(t')\,|\psi(t')\rangle} , \tag{12.55}$$

which is the Lippmann-Schwinger Equation for $|\psi(t)\rangle$. By iteration we get

$$\begin{aligned} |\psi_I(t)\rangle &= |\psi_I(t_0)\rangle - \tfrac{i}{\hbar}\int_{t_0}^{t} dt' \; V_I(t')\,|\psi_I(t_0)\rangle \\ &\quad +(-\tfrac{i}{\hbar})^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \; V_I(t')V_I(t'')|\psi_I(t_0)\rangle + ... \qquad (12.56) \\ &= \widehat{T} e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' V_I(t')}|\psi_I(t_0)\rangle \qquad (12.57) \\ &= U_I(t,t_0)|\psi_I(t_0)\rangle. \qquad (12.58) \end{aligned}$$

The state in the Schrödinger picture is, hence, obtained as

$$\begin{aligned} |\psi_s(t)\rangle &= U_s^0(t,t_0)\, U_I(t,t_0)\, |\psi_I(t_0)\rangle & (12.59)\\ &= e^{-\frac{i}{\hbar}H^0(t-t_0)}\, \widehat{T}\, e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' V_I(t')}\, |\psi_I(t_0)\rangle & (12.60) \end{aligned}$$

where

$$|\psi_I(t_0)\rangle = |\psi_s(t_0)\rangle. \tag{12.61}$$

This equation allows to calculate the time evolution of any state under the action of $V(t)$. In particular, an (initial) eigenstate $|i^0\rangle$ of H^0 will, after time t, have developed into a superposition of final eigenstates $|f^0\rangle$.

$$|\psi_s(t)\rangle = \sum_m |f^0\rangle\langle f^0\,|\,\psi_s(t)\rangle, \quad |\psi(t_0)\rangle = |i^0(t_0)\rangle, \tag{12.62}$$

where $\langle f^0(t)\,|\,\psi_s(t)\rangle$ is on the one hand the amplitude for finding the system in eigenstate $|f^0(t)\rangle$ of H^0, after $V(t)$ has been acting for the time t on the initial state $|i^0\rangle$ and on the other hand the transition amplitude for $|i^0\rangle \longrightarrow |f^0\rangle$ after the time t under the action of $V(t)$.

$\langle f^0\,|\,\psi_s(t)\rangle$ can be calculated using perturbation theory. In first order perturbation theory, set $t_0 = 0$, i.e.

$$|\psi_s(0)\rangle = |i^0(0)\rangle, \tag{12.63}$$

and get by this

$$\begin{aligned} |\psi_s(t)\rangle &= e^{-\frac{i}{\hbar}H^0 t}\{\, |i^0(0)\rangle - \tfrac{i}{\hbar}\textstyle\int_0^t dt'\; V_I(t')|i^0(0)\rangle\,\} & (12.64)\\ \langle f^0(t)\,|\,\psi_s(t)\rangle &= \langle f^0(t)|e^{-\frac{i}{\hbar}H^0 t}|i^0(0)\rangle \\ &\quad -\tfrac{i}{\hbar}\textstyle\int_0^t dt'\; \langle f^0(t)|e^{-\frac{i}{\hbar}H^0 t}V_I(t')|i^0(0)\rangle & (12.65)\\ &= \langle f^0(0)|i^0(0)\rangle - \tfrac{i}{\hbar}\textstyle\int_0^t dt'\; \langle f^0(t)|V_I(t')\,|i^0(0)\rangle, & (12.66) \end{aligned}$$

i.e.

$$\boxed{\langle f^0(t)\,|\,\psi_s(t)\rangle = \delta_{fi} - \tfrac{i}{\hbar}\textstyle\int_0^t dt'\; \langle f^0(0)|\,V_I(t')\,|i^0(0)\rangle =: d_{fi}(t)}\,. \tag{12.67}$$

This is the first order transition rate $|i^0\rangle \to |f^0\rangle$ after time t. With

$$V_I(t') = e^{\frac{i}{\hbar}H^0 t'}\, V_s(t')\, e^{-\frac{i}{\hbar}H^0 t'} \tag{12.68}$$

equation (12.67) becomes

$$\boxed{d_{fi}(t) = \delta_{fi} - \tfrac{i}{\hbar}\int_0^t dt'\ \langle f^0(0)|\, V_s(t')\, |i^0(0)\rangle\ e^{-\frac{i}{\hbar}(E_i^0 - E_f^0)\, t'}}\ . \tag{12.69}$$

12.3 Periodic perturbation to first order perturbation theory

Consider a periodic perturbation

$$V_s(t) = \widehat{V}\cos(\omega t), \tag{12.70}$$

which is the real part of the potential $\widehat{V}e^{-i\omega t}$ with $\omega \longrightarrow \pm\omega$. Assume that the system comes into contact with the perturbation at time $t = 0$.

$$\begin{aligned} d_{fi}(t) &= -\tfrac{i}{\hbar}\int_0^t dt'\ \langle f^0(0)|\, \widehat{V}\, |i^0(0)\rangle \exp\left(\tfrac{i}{\hbar}(E_f - E_i - \hbar\omega)t'\right) && (12.71)\\ &= -\tfrac{i}{\hbar}\langle f^0|\, \widehat{V}\, |i^0\rangle \tfrac{\exp\left(i(\omega_f - \omega_i - \omega)t\right) - 1}{i(\omega_f - \omega_i - \omega)}, && (12.72) \end{aligned}$$

with

$$f \neq i \quad \text{and} \quad \omega_{f,i} = \tfrac{E_{f,i}^0}{\hbar}. \tag{12.73}$$

The probability for the transition $|i^0\rangle \to |f^0\rangle$ reads

$$P_{i\to f}(t) = |d_{fi}|^2 = \tfrac{1}{\hbar^2}|\langle f^0|\, \widehat{V}\, |i^0\rangle|^2 \left[\tfrac{\sin\left(1/2\cdot(\omega_f - \omega_i - \omega)t\right)}{1/2\cdot(\omega_f - \omega_i - \omega)t}\right]^2 t^2, \tag{12.74}$$

see also figure 12.2.

Transition dynamics:
The system "likes" to go to states with $|x| \lesssim \pi$,

$$\begin{aligned} |(\omega_f - \omega_i - \omega)\tfrac{t}{2}| &\lesssim \pi && (12.75)\\ E_f^0 - E_i^0 &= \hbar\omega + \Delta && (12.76)\\ -\tfrac{2\pi\hbar}{t} &\leqslant \Delta \leqslant \tfrac{2\pi\hbar}{t}. && (12.77) \end{aligned}$$

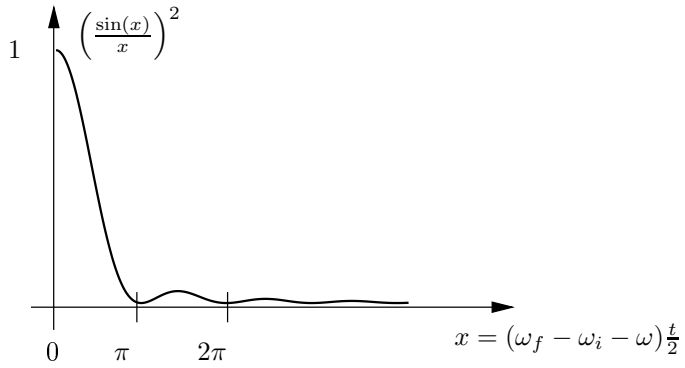

Figure 12.2: Illustration of the transition probability

Discussion:
The allowed energy interval Δ around $\hbar\omega$ shrinks to 0 with increasing time, because for finite time t, the perturbation is a pulse $[\,0, t\,]$, whose Fourier spectrum contains a continuum of frequencies in the interval $[\,\omega - \frac{2\pi}{t}, \omega + \frac{2\pi}{t}\,]$.

Energy conservation rule:
$E_f^0 = E_i^0 + \hbar\omega$ applies, when the width (uncertainty) of the spectrum $2\pi/t$ is negligible towards its center frequency ω , i.e. for $\frac{2\pi}{t} \ll \omega$ and many cycles in the pulse

$$\boxed{\omega t \gg 2\pi} \tag{12.78}$$

is valid. The transition amplitude for t $\rightarrow \infty$ reads

$$\begin{aligned} d_{fi}(\infty) &= \lim_{t\to\infty} -\tfrac{i}{\hbar}\int_{-\frac{t}{2}}^{\frac{t}{2}} dt' \langle f^0(0)|\,\widehat{V}\,|i^0(0)\rangle (\, e^{i(\omega_f-\omega_i-\omega)t'} + e^{i(\omega_f-\omega_i+\omega)t'}\,) \\ &= -\tfrac{2\pi i}{\hbar}\langle f^0|\,\widehat{V}\,|i^0\rangle [\,\delta(\omega_f-\omega_i-\omega) + \delta(\omega_f-\omega_i+\omega)\,], \end{aligned}$$

and the transition probability

$$P_{fi}(\infty) = \tfrac{4\pi^2}{\hbar^2}|\langle f^0|\,\widehat{V}\,|i^0\rangle|^2\,[\,\delta(\omega_f-\omega_i-\omega)\,]^2 + [\,\delta(\omega_f-\omega_i+\omega)\,]^2 \tag{12.79}$$

with

$$\begin{aligned} & \delta(\omega_f - \omega_i - \omega)\,\delta(\omega_f - \omega_i - \omega) \\ = \;& \delta(\Delta\omega_{fi} - \omega)\,\delta(\Delta\omega_{fi} - \omega) && (12.80) \\ = \;& \delta(\Delta\omega_{fi} - \omega)\frac{1}{2\pi}\lim_{t\to\infty}\int_{-\frac{t}{2}}^{\frac{t}{2}} e^{i(\Delta\omega_{fi}-\omega)}\,dt' && (12.81) \\ = \;& \delta(\Delta\omega_{fi} - \omega)\lim_{t\to\infty}\frac{t}{2\pi}. && (12.82) \end{aligned}$$

The transition rate for long times,

$$\delta(\omega_f - \omega_i - \omega) = \hbar\delta(E_f^0 - E_i^0 - \hbar\omega), \tag{12.83}$$

reads

$$\boxed{R_{i\to f} = \frac{P_{i\to f}}{t} = \frac{2\pi}{\hbar}|\langle f^0|\widehat{V}|i^0\rangle|^2\delta(E_f^0 - E_i^0 \mp \hbar\omega)} \;. \tag{12.84}$$

Equation (12.84) is called *Fermi's Golden Rule.*

Remarks:

- In realistic problems, the final state energy E_f^0 is always integrated over a finite range dE_f so that the transition becomes

  $$R_{i\to f}(E_f)\,dE_f = \frac{2\pi}{\hbar}|\langle f^0|\,\widehat{V}\,|i^0\rangle|^2 N(E_i^0 + \hbar\omega)\,dE_f, \tag{12.85}$$

  where the factor $N(E_i^0 + \hbar\omega)$ is the density of states in the final state.

- Fermi's Golden Rule is only valid for not too large times t, since then higher order contributions of perturbation theory become important. If the system has a discrete eigenspectrum, the time evolution is eventually periodic, e.g. neutrino oscillations, 2d-Hilbert space. Fermis' Golden Rule remains valid, as long as the occupation probability of the initial state is much greater than the occupation probability of the final state. This is, in particular, the case, if the final state is depopulated into a 3rd state.

Derivation of Fermis's Golden Rule:

- For $t > \frac{2\pi\hbar}{|E_f - E_i|}$ a transition to the whole ensemble of final states is possible. In this case, all states are in the central peak of $\sin^2\left(\frac{\omega}{2}t\right)/(\omega/2)$. In other words, the energy width dE is so large, that the central peak is within dE. Only then the approximation $2\pi t\delta(\omega)$ is valid.

- For t not being too large the distance between the energy of the final states is small for a sufficiently dense distribution, since ω is a continuous variable. If δE denotes their distance, we, hence, get

$$t \ll \frac{2\pi\hbar}{\delta E}. \tag{12.86}$$

- Validity of first order perturbation theory: $Rt \ll 1$

$$\frac{2\pi\hbar}{\Delta E} < t \ll \begin{cases} \frac{2\pi\hbar}{\delta E} \\ R^{-1} \end{cases} \tag{12.87}$$

Characteristic function:

$$\begin{aligned} \| \chi_{[-t,t]} \|^2 &= \int \chi_{[-t,t]}\, dx = 2t = \| F\chi_{[-t,t]} \|^2 && (12.88)\\ F\chi &= \tfrac{1}{\sqrt{2\pi}} \int_{-t}^{t} e^{-i\omega x}\, dx = \tfrac{1}{\sqrt{2\pi}} \tfrac{e^{-i\omega t} e^{i\omega t}}{-i\omega} && (12.89)\\ &= \sqrt{\tfrac{2}{\pi}} \tfrac{\sin\omega t}{\omega} && (12.90)\\ \Rightarrow \int (\tfrac{\sin\omega t}{\omega})\, d\omega &= \pi t && (12.91) \end{aligned}$$

12.4 Sudden perturbation

A sudden perturbation is reprensented by an abrupt change of the Hamiltonian over a small time interval ε. The change of state according to the Schrödinger equation has the following asymptotic behavior.

$$\begin{aligned} |\psi_s(+\tfrac{\varepsilon}{2})\rangle - |\psi_s(-\tfrac{\varepsilon}{2})\rangle &= |\psi_{\text{after}}(t)\rangle - |\psi_{\text{before}}(t)\rangle && (12.92)\\ &= -\tfrac{i}{\hbar} \int_{-\frac{\varepsilon}{2}}^{\frac{\varepsilon}{2}} dt\; H(t)\, |\psi_s(t)\rangle && (12.93)\\ &\to 0, && (12.94) \end{aligned}$$

for $\varepsilon \to 0$. Therefore, the state is not changed by a finite, sudden perturbation.

Figure 12.3: Sudden perturbation

The approximation of a discontinuous change is good, if the time scale of the perturbation change ε, is short compared to the characteristic time scale τ on which $|\psi_s(t)\rangle$ changes, i.e.

$$\begin{aligned} & |\psi_s(\tfrac{\varepsilon}{2})\rangle - |\psi_s(-\tfrac{\varepsilon}{2})\rangle \\ \cong\ & -\left[\tfrac{i}{\hbar}\int_{-\frac{\varepsilon}{2}}^{\frac{\varepsilon}{2}} dt\, H(t)\right] \cdot |\psi(0)\rangle \qquad (12.95) \\ \approx\ & -i \underbrace{\varepsilon \cdot \omega_{\text{char}}}_{\ll 1} |\psi(0)\rangle \qquad (12.96) \end{aligned}$$

Example: β decay

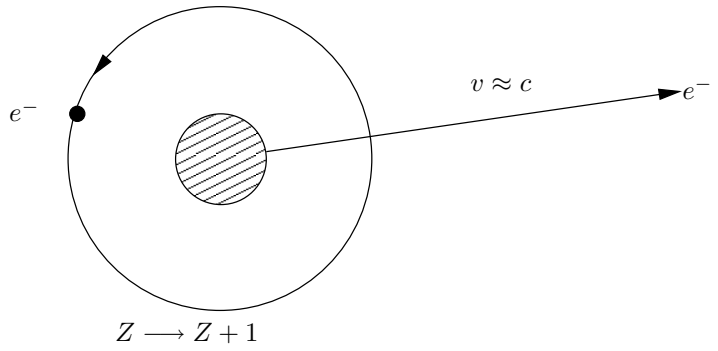

Figure 12.4: Nuclear change at β decay

Here, an abrupt change of nuclear charge, $Z \to Z+1$, during the time

$$\varepsilon = \frac{a_0}{Zc} = \frac{\text{atom radius}}{\text{velocity of } e^-} \qquad (12.97)$$

takes place where a_0 is the Bohr radius of the hydrogen atom,

$$a_0 = \frac{\hbar^2}{me^2}. \qquad (12.98)$$

For $Z > 1$ one gets

$$a = \tfrac{\hbar^2}{mZe^2}. \tag{12.99}$$

The energy eigenvalue is given by

$$E_n = \frac{ZRy}{n^2} \tag{12.100}$$

with the Rydberg constant

$$1\text{Ry} = \frac{me^4Z^2}{2\hbar^2} = \frac{Z^2e^2}{2a_0}. \tag{12.101}$$

Characteristic time for the 1s electron:

$$\tau \approx \frac{\hbar}{E_0} \approx \frac{2\hbar a_0}{Z^2e^2} \tag{12.102}$$

$$\frac{\varepsilon}{\tau} = \frac{1}{2}Z\frac{e^2}{\hbar c} = \frac{1}{2}Z\alpha = \frac{1}{274}Z, \tag{12.103}$$

which is a small number for light nuclei.

After the perturbation is switched on, the system is not in an eigenstate of the perturbed Hamiltonian. It evolves according to the perturbed, time independent Hamiltonian, with the initial condition that at $t = 0$ the system was in an eigenstate of the unperturbed Hamiltonian.

Sudden perturbation:

$$d_{fi} = -\tfrac{i}{\hbar}\left\langle f^0\right|\widehat{V}\left|i^0\right\rangle \tfrac{\exp\left(i(\omega_f-\omega_i)t\right)-1}{i(\omega_f-\omega_i)} \tag{12.104}$$

$$\Rightarrow P_{fi} = \tfrac{1}{\hbar^2}\left|V_{fi}\right|^2 \tfrac{\sin\frac{\Delta\omega}{2}t}{\frac{\omega}{2}t} \tag{12.105}$$

$$\underset{t\to\infty}{\Rightarrow} P_{fi} = \tfrac{t}{2\pi}\tfrac{4\pi^2}{\hbar^2}\left|V_{fi}\right|^2\delta(\omega_f-\omega_i) \tag{12.106}$$

$$= \frac{t}{2\pi}\frac{4\pi^2}{\hbar^2}\left|V_{fi}\right|^2\hbar\delta\left(E_f-E_i\right) \quad \text{"elastic"} \tag{12.107}$$

$$\Rightarrow R_{fi} = \frac{P_{fi}}{t} \tag{12.108}$$

Adiabatic perturbation:

$$V(t) = e^{\eta t} V \qquad , \eta > 0 \tag{12.109}$$

$$\Rightarrow P_{fi} = \frac{1}{\hbar^2} \left| \int_{t_0}^{t} d\tau \; e^{\eta \tau} \, e^{\frac{i}{\hbar}(E_f - E_i)\tau} \langle f | \, V \, | i \rangle \right|^2 \tag{12.110}$$

$$\underset{t_0 \to -\infty}{\Rightarrow} P_{fi} = \left| \frac{e^{\eta t} \, e^{\frac{i}{\hbar}(E_f - E_i)t}}{E_f - E_i - i\eta\hbar} \right|^2 |V_{fi}|^2 \tag{12.111}$$

$$= \frac{e^{2\eta t}}{(E_f - E_i)^2 + (\eta\hbar)^2} \, |V_{fi}|^2 \tag{12.112}$$

$$\Rightarrow \frac{\partial P_{fi}}{\partial t} = e^{2\eta t} \, \frac{2\eta}{(E_f - E_i)^2 + (\eta\hbar)^2} \, |V_{fi}|^2 \tag{12.113}$$

$$\underset{\eta \to 0}{\Rightarrow} R_{fi} = \frac{\partial P_{fi}}{\partial t} = e^{2\eta t} \, \frac{2\pi}{\hbar} \, \delta(E_f - E_i) \, |V_{fi}|^2 \tag{12.114}$$

12.5 Adiabatic perturbation

Adiabatic theorem:
If $H(t)$ changes on a time scale T much slower than the intrinsic time scales of the system τ , especially the inverse eigenenergies $\hbar/E_n^0$, then the system makes many cycles $\exp\left(-\frac{i}{\hbar} E_n T\right)$ before $H(t)$ changes significantly, and we can define stationary eigenstates and eigenenergies at each instant of time, $|\psi_n(t)\rangle$. The time dependent eigenstates of $H(t)$ are the energy eigenstates of $H(t)$ at each instant of time.

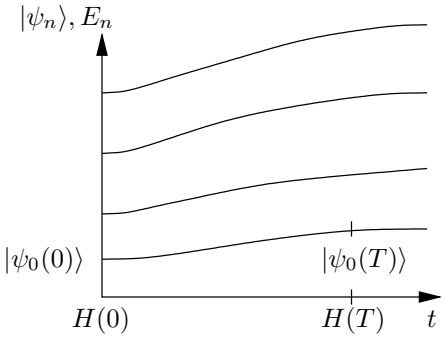

Figure 12.5: Adiabatic evolution of the eigenenergies, eigenstates

Therefore the system does not change if it is in a state of the discrete spectrum.

Example: Particle in a slowly expanding box

- Time for one oscillation of the particle reads

$$\tau = \frac{L}{v} = \frac{mL}{p} = \frac{mL^2}{\hbar\pi}, \tag{12.115}$$

since $p = \hbar\pi/L$ and $v = p/m = \hbar/mL$. It is adiabatic if

$$\frac{|\Delta L| \text{ per cycle } \tau}{L} \cong \frac{|\frac{\partial L}{\partial t}|mL^2}{\hbar L} = \frac{mL}{\pi\hbar}|\frac{\partial L}{\partial t}| \ll 1 \tag{12.116}$$

or

$$\frac{v_{walls}}{v_{particle}} \ll 1. \tag{12.117}$$

- Eigenenergies

$$E_n^0 = \frac{p_n^2}{2m} = \frac{(n\hbar\pi)^2}{2mL^2} \tag{12.118}$$

$$E_f^0 - E_i^0 \approx \frac{(\hbar\pi)^2}{mL^2} \tag{12.119}$$

$$\tau = \frac{\hbar}{E_f^0 - E_i^0} \approx \frac{mL^2}{\hbar\pi^2} \tag{12.120}$$

Chapter 13

Many-Particle Systems - Fermions, Bosons

13.1 Many-particle wave functions

Assume a system of N identical particles which do not interact with each other. The full Hamiltonian then reads

$$H = H^1(\vec{x}_1, \vec{p}_1) + H^1(\vec{x}_2, \vec{p}_2) + ... + H^1(\vec{x}_N, \vec{p}_N), \tag{13.1}$$

where the single-particle Hamiltonian in x-representation is given by

$$H^1(\vec{x}, \vec{p}) = \frac{\vec{p}^2}{2m} + V(\vec{x}) \tag{13.2}$$

with $\vec{x}_1, \vec{p}_1$ being the coordinate and the momentum of particle 1 and so on.
Then the state can be written as a direct product of the single-particle states. Let particle i, $i = 1, ..., N$, be in eigenstate $|n_i\rangle$ of the Hamiltonian H^1. Then try to construct the many-particle state.

$$|\psi(x_1, ..., x_N)\rangle = |\psi_{n_1}(\vec{x}_1)\rangle \, |\psi_{n_2}(\vec{x}_2)\rangle \, ... \, |\psi_{n_N}(\vec{x}_N)\rangle \tag{13.3}$$

Quantum Mechanics:
If all the N particles are indistinguishable, then the state can only be changed by a phase factor when two particles are interchanged, i.e. $\vec{x}_i \leftrightarrow \vec{x}_j$. Exchanging these particle twice must lead back to the initial state. Therefore the phase factor aquired by particle exchange must be ± 1 (representation of the permutation

group). Hence, the many-particle wave function is either totally symmetric or totally antisymmetric.

Symmetric wave functions: **Bosons**

$$\begin{aligned} & |\psi(x_1,\ldots,x_N)\rangle_B \\ = \; & \sqrt{\tfrac{N_1!\ldots N_N!}{N!}} \sum_{p\{\vec{x}_1,\ldots,\vec{x}_N\}} |\psi_{n_1}(\vec{x}_1)\rangle \ldots |\psi_{n_N}(\vec{x}_N)\rangle \end{aligned} \tag{13.4}$$

Antisymmetric wave functions: **Fermions**

$$\begin{aligned} & |\psi(x_1,\ldots,x_N)\rangle_F \\ = \; & \tfrac{1}{\sqrt{N!}} \sum_{p\{\vec{x}_1,\ldots,\vec{x}_N\}} (-1)^p |\psi_{n_1}(\vec{x}_1)\rangle \ldots |\psi_{n_N}(\vec{x}_N)\rangle \end{aligned} \tag{13.5}$$

N_i is the number of particles in the single-particle state i and the exponent p is the permutation factor which can assume the values ± 1 according to an even (+1) or an odd (-1) permutation.

Example: 2 particles

Bosons:

$$|\psi(x_1,x_2)\rangle_B = \frac{1}{\sqrt{2}}[\,|\psi_1(\vec{x}_1)\rangle|\psi_2(\vec{x}_2)\rangle + |\psi_1(\vec{x}_2)\rangle|\psi_2(\vec{x}_1)\rangle\,] \tag{13.6}$$

Fermions:

$$|\psi(x_1,x_2)\rangle = \frac{1}{\sqrt{2}}[\,|\psi_1(\vec{x}_1)\rangle|\psi_2(\vec{x}_2)\rangle - |\psi_1(\vec{x}_2)\rangle|\psi_2(\vec{x}_1)\rangle\,] \tag{13.7}$$

$$= \begin{vmatrix} |\psi_1(\vec{x}_1)\rangle & |\psi_1(\vec{x}_2)\rangle \\ |\psi_2(\vec{x}_1)\rangle & |\psi_2(\vec{x}_2)\rangle \end{vmatrix} \tag{13.8}$$

For N particles we get the so-called *Slater determinant*,

$$|\psi(x_1,...,x_N)\rangle = \begin{vmatrix} |\psi_{n_1}(\vec{x}_1)\rangle & \cdots & |\psi_{n_1}(\vec{x}_N)\rangle \\ |\psi_{n_2}(\vec{x}_1)\rangle & \cdots & |\psi_{n_2}(\vec{x}_N)\rangle \\ \vdots & & \vdots \\ |\psi_{n_N}(\vec{x}_1)\rangle & \cdots & |\psi_{n_N}(\vec{x}_N)\rangle \end{vmatrix}. \tag{13.9}$$

Spin-Statistics theorem:
Systems consisting of identical particles with integer spin have totally symmetric wave functions (Bosons). Systems consisting of identical particles with half-integer spin have totally antisymmetric wave functions (Fermions).
This theorem follows from relativistic quantum field theory and is only mentioned here without a proof and any motivation.

Slater determinant:
If two particles occupy the same state, $n_i = n_j$ for two particles, then the state is 0. Therefore no double occupancy of states is possible.

13.2 Helium atom

The Helium atom consists of two electrons which have to obey the Pauli principle.

Spin eigenfunctions:

$$\chi_{00} = \tfrac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \quad s=0 \quad \text{antisymmetric} \tag{13.10}$$
$$\chi_{11} = \uparrow\uparrow \tag{13.11}$$
$$\chi_{10} = \tfrac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \quad s=1 \quad \text{symmetric} \tag{13.12}$$
$$\chi_{1-1} = \downarrow\downarrow \tag{13.13}$$

Space eigenfunctions:
From the full Hamiltonian,

$$H = \frac{1}{2m}\left(\vec{p}^{(1)^2} + \vec{p}^{(2)^2} - \frac{Ze^2}{r^{(1)}} - \frac{Ze^2}{r^{(2)}} + \frac{e^2}{|r^{(1)} - r^{(2)}|}\right), \tag{13.14}$$

we can see that the problem separates so that we choose as an ansatz for the eigenfunctions

$$\phi = \phi_{n_1 l_1 m_1}(\vec{r}^{(1)})\ \phi_{n_2 l_2 m_2}(\vec{r}^{(2)}). \tag{13.15}$$

For the ground-state we get the energy

$$E_0 = -2\frac{Z^2 e^2}{2a_0} \tag{13.16}$$

and the symmetric state $\phi_{100}\ \phi_{100}\,(L=0)$. For the first excited state we get

$$E_1 = \left(-1-\frac{1}{4}\right)\frac{Z^2e^2}{2a_0} \tag{13.17}$$

and the state $\phi_{100}\ \phi_{2lm}$ or $\phi_{2lm}\ \phi_{100}\,(L=l)$.

We therefore have a well-defined symmetry in this problem,

$$\phi^{\pm} = \frac{1}{\sqrt{2}}(\phi_{100}\ \phi_{2lm} \pm \phi_{2lm}\ \phi_{100}), \tag{13.18}$$

where the $\pm$ indicates the behavior under exchange.

Altogether we have the ground state

$$\phi_{100}\ \phi_{100}\ \chi_{00}, \qquad s=0 \tag{13.19}$$

and the first excited states

$$\psi^{\text{para}} = \phi_l^+\chi_{00} \quad \text{or} \quad \psi^{\text{ortho}} = \phi_l^-\chi_{1m_s}. \tag{13.20}$$

The Ortho-Helium has no ground state and the wave function ψ^{ortho} is metastable. It also has a fine structure.

$\rightarrow$ Are there two sorts of Helium?!

Repulsion: Level spacing $\sim 0,1\text{eV}$

Hund's rules
They take the repulsion into account.

(1.) S maximal:
The spin function is symmetric and for strong repulsion the spin function is antisymmetric, in particular $=0$ for $\vec{r}^{(i)} \rightarrow \vec{r}^{(j)}$.

(2.) L maximal:
The electrons are further away from the nucleus and therefore further away from each other. Hence, the repulsion is smaller. This effect is smaller than the first rule.

(3.) If the shell is less than half-filled, then $J = |L - S|$ and if the shell is more than half-filled $J = L + S$, because of LS-coupling. The ^{2}He ground state has $S = 0$ and not $S = 1$.

Relativistic corrections:

$$-\frac{p^4}{8m^3e^2} \rightarrow -\frac{mc^2(Z\alpha)^4}{2m^4}\left(\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right), \tag{13.21}$$

$$\frac{Ze^2}{2m^2c^2r^3}\,\vec{L}\cdot\vec{S} \rightarrow \frac{me^2(Z\alpha)^4}{4n^3l(l+\frac{1}{2})(l+1)}\left\{\begin{array}{c} l \\ -l-1 \end{array}\right\} \tag{13.22}$$

$$\text{and } = 0 \quad \text{for} \quad l = 0 \tag{13.23}$$

$$\frac{\hbar^2Ze^2}{2m^2c^2}\,\delta(\vec{r}) \rightarrow \frac{mc^2(Z\alpha)^4}{2n^4}\,\delta_{2,0} \tag{13.24}$$

$$\Rightarrow L' = \frac{mc^2(Z\alpha)^4}{2n^4}\left(\frac{3}{4} - \frac{n}{j+\frac{1}{2}}\right) \tag{13.25}$$

13.3 Hund's rules: Antisymmetry of the total wave function

(1.) Total spin: S maximal

- Spin-wave function totally symmetric

→ Position wave function totally antisymmetric

→ $\psi(\vec{r}_i, \vec{r}_j) = 0$ for $\vec{r}_i = \vec{r}_j$

→ Minimization of Coulomb energy of electrons

(2.) Total orbital angular momentum: L maximal

- Wave function most be strongly extended in space

→ Maximal average distance between electrons

→ Coulomb-energy due to $e^- - e^-$ interaction minimized

(3.) Total angular momentum

$$J = \left\{\begin{array}{ll} L+S & \text{shell less than half filled} \\ L-S & \text{more} \end{array}\right. \tag{13.26}$$

$$V_{SB} = \sum_{i=1}^{N} \alpha_i \vec{L}_i \cdot \vec{S}_i \text{ (Russel-Saunders)} \tag{13.27}$$

$$\alpha_i \cong \frac{\hbar^2}{2m^2c^2}\frac{Ze^2}{r^3} > 0$$
(without interaction corrections) (13.28)

From the first two rules we get

$$\langle \vec{L}_i \rangle \sim \langle \vec{L} \rangle, \quad \langle \vec{S}_i \rangle \sim \langle \vec{S} \rangle \tag{13.29}$$

such that

$$V_{SB} = A \cdot \vec{S} \cdot \vec{L} = \frac{1}{2} A[J(J+1) - L(L+1) - S(S+1)]. \tag{13.30}$$

- Shell less than half filled: All spins $\uparrow\uparrow\uparrow$

$$S_i = \frac{S}{N} \tag{13.31}$$

$$V_{SB} = \sum_{i=1}^{N} \alpha_i \vec{L}_i \cdot \frac{S}{N} \cong \frac{\alpha}{N} \vec{L} \cdot \vec{S} \tag{13.32}$$

$$A = \frac{\alpha}{N} > 0 \tag{13.33}$$

  $\Rightarrow$ J minimal: $J = |L - S|$

- Shell more than half filled:
  Substract V_{SB} from filled shell $A < 0$

13.4 Atoms with several electrons - periodic system of elements

With increasing number of electrons the orbitals of an atom $R_{nl}(\vec{r})Y_l^m(\theta, \varphi)$ are filled in the ground state according to

- Minimize energy (lowest-lying orbitals)
- Pauli principle (fermions)
- Hund's rules (minimizing energy, taking corrections by Coulomb-interaction and spin-orbit coupling into account)

Shell structure:

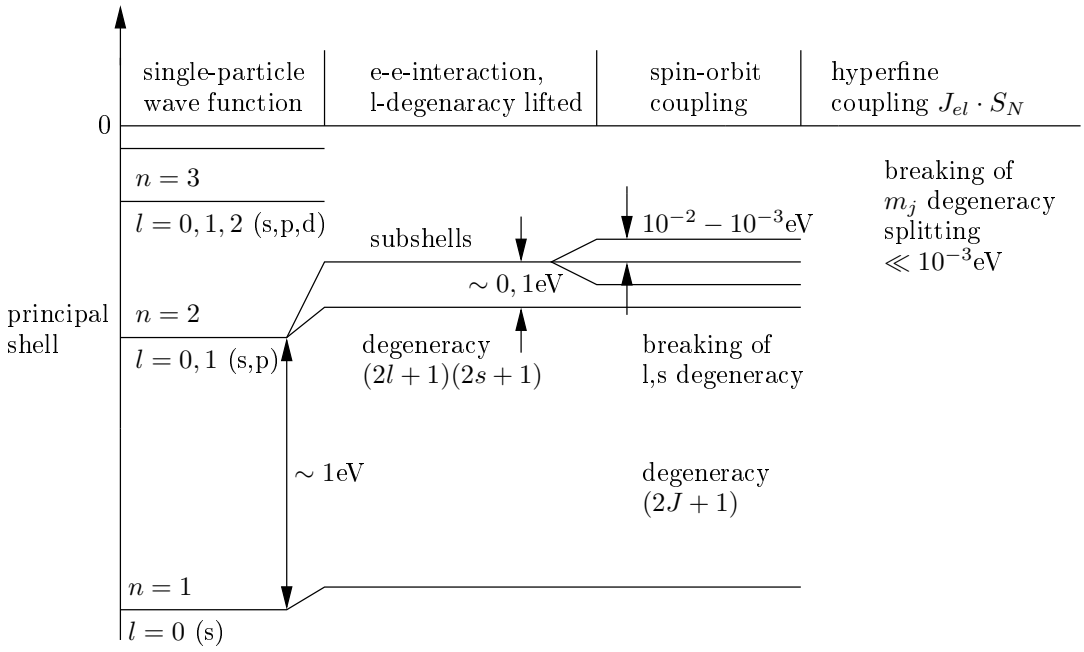

Figure 13.1: Split up of energy states

Periodic system of elements[1]

Electronic configurations of elements:

- 8 elements per main period:
  Filling of (nearby degenerate s, p orbitals)
- Noble gases:
  Filled main shells. Stable, since large energy gap to next main shell.
- Transition metal elements:
  Filling of d-shell ($l = 2$, for $n \geq 3$)
  $2(2l + 1) = 10$ degeneracy
- Lauthanides, actinides:
  Filling of $4f$ and $5f$ shells ($l = 3$, for $n \geq 4$)
  $2(2l + 1) = 14$ degeneracy

[1] see e.g. http://www.webelements.com or http://www.chemistrycoach.com/periodic_tables.htm

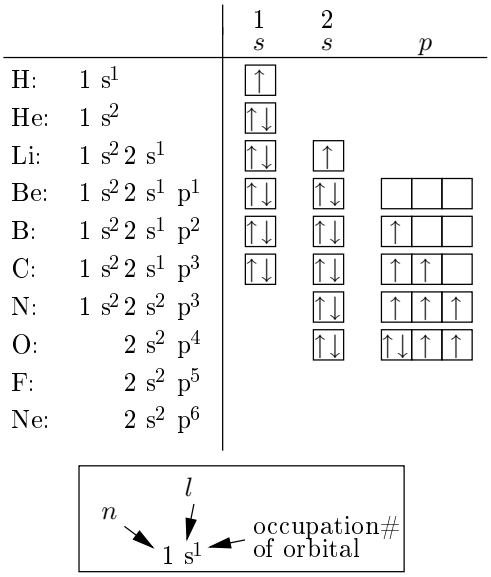

Figure 13.2: Electronic configurations of elements

13.5 The Fermi sea

Consider electrons in a box of length L and volume L^3. The possible $\vec{k}$-states read

$$\vec{k} = \frac{2\pi}{L}(n_x\widehat{e}_x + n_y\widehat{e}_y + n_z\widehat{e}_z), \quad n_i = 0, \pm 1, \pm 2. \tag{13.34}$$

The states are filled according to the Pauli principle. The k-space volume for two electrons (spin $\uparrow, \downarrow$) is $(\frac{2\pi}{L})^3$.

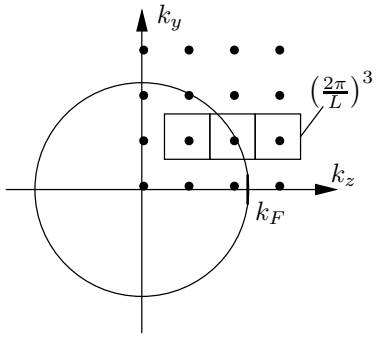

Figure 13.3: Illustration of the Fermi sea

The Fermi momentum and the Fermi energy are given by

$$P_F = \hbar k_F, \quad E_F = \frac{p_F^2}{2m}. \tag{13.35}$$

A sharp edge separates occupied from unoccupied states.

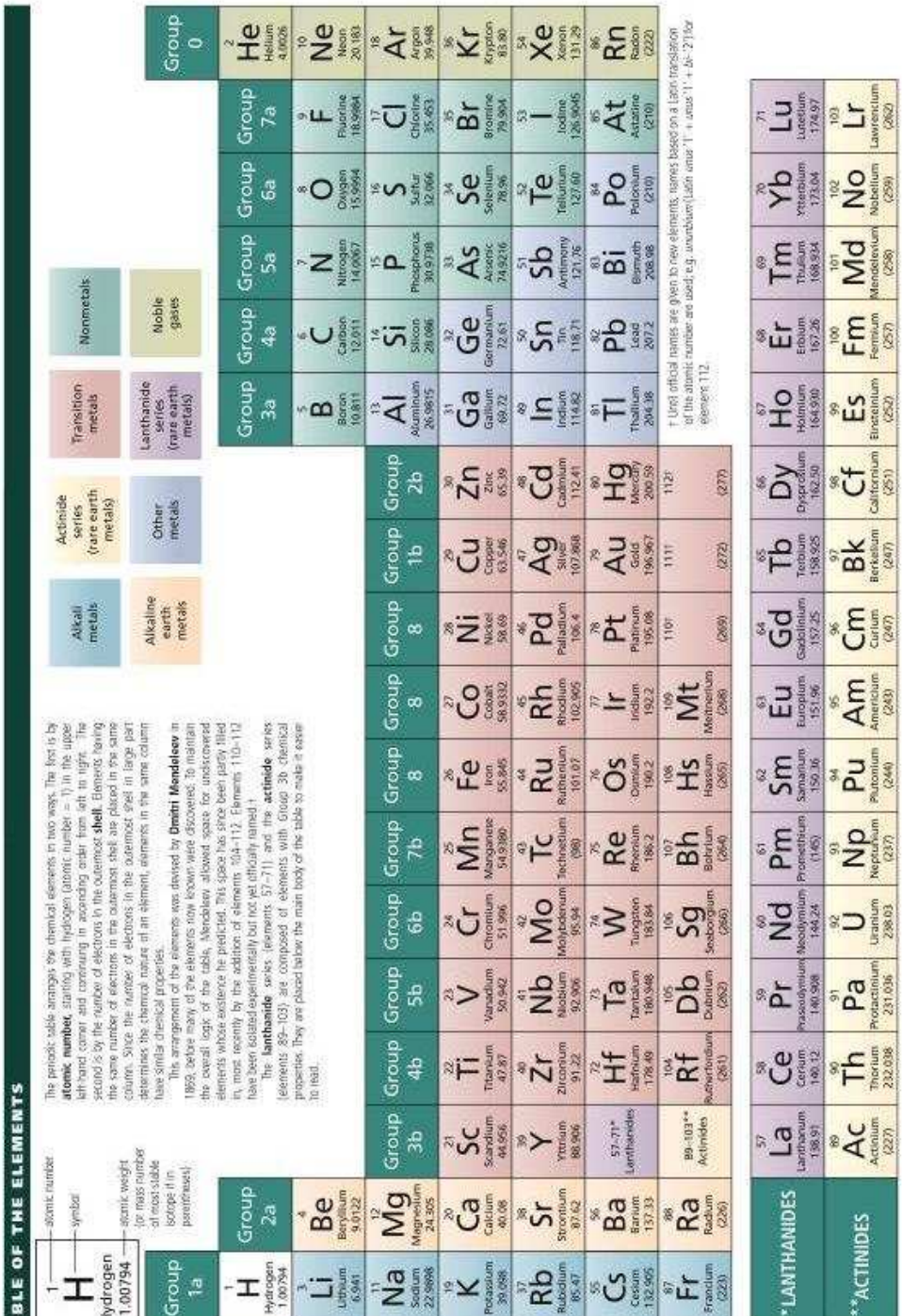

Figure 13.4: The periodic system of elements (Source: http://www.bartleby.com/61/charts/A4elemen.html)

Chapter 14

Electrons in Electromagnetic Fields

14.1 Atoms interacting with electromagnetic radiation; classical treatment of the e-m field

In an atom the eigenstates are stationary (time-dependence $\sim \exp\left(-\frac{i}{\hbar}E_n t\right)$). This remains true even for time-independent perturbations, since these would only modify the stationary eigenstates.
Thus, in order to have transitions between atomic states (excitations, decay) a time-dependent perturbation is necessary.
Consider a time-dependent external electromagnetic field with radiative transitions like

$$\vec{A}(\vec{r},t) = \vec{A}_0 \cos(\vec{k}\vec{r} - \omega t), \tag{14.1}$$

which represents a plane wave. From

$$H = \frac{1}{2m}\left(\vec{p} - \frac{(-e)}{c}\vec{A}\right)^2, \quad \vec{\nabla}\vec{A} = 0 \tag{14.2}$$

we have the perturbation linear in $\vec{A}$ (also see section 9.2).

$$\begin{aligned} V(\vec{r},t) &= \frac{e}{mc}\vec{A}\cdot\vec{p} && (14.3)\\ &= \frac{e}{mc}\cos(\vec{k}\vec{r} - \omega t)\vec{A}_0\cdot\vec{p} && (14.4)\\ &= \frac{e}{2mc}\left(e^{i(\vec{k}\vec{r}-\omega t)} + e^{-i(\vec{k}\vec{r}-\omega t)}\right)\vec{A}_0\cdot\vec{p} && (14.5)\\ &= V^+ e^{-i\omega t} + V^- e^{i\omega t} && (14.6) \end{aligned}$$

The transition rate from the initial eigenstate $|i^0\rangle$ to the final eigenstate $|f^0\rangle$ of the unperturbed Hamiltonian follows from Fermi's Golden rule,

$$\begin{aligned} R_{i\to f} &= \frac{2\pi}{\hbar}\{\,|\langle f^0\,|V^+|\,i^0\rangle|^2\,\delta(E_f^0 - E_i^0 - \hbar\omega) \\ &\quad +|\langle f^0\,|V^-|\,i^0\rangle|^2\,\delta(E_f^0 - E_i^0 + \hbar\omega)\,\}. \end{aligned} \tag{14.7}$$

14.1.1 Photoelectric effect

The photoelectric effect describes the ionization of an atom by electromagnetic radiation. The initial state $|i^0\rangle$ is a bound eigenstate of the atom, e.g. the ground state. The final state $|f^0\rangle \approx |\vec{p}_f\rangle$ is an approximately free state (momentum $\vec{p}_f$[1]).

The approximation of a free final state $|\vec{p}_f\rangle$ is good if the "higher order terms" give a small contribution to $|\langle f^0\,|V^\pm|\,i^0\rangle|^2$ compared to $|\vec{p}_f\rangle$.

This is the case if

- $E_f^0 \gg E_i^0$,
- the initial state is a s-wave (e.g. the H ground state).

Since for absorption $E_f^0 - E_i^0 > 0$ yields, only the first term in $R_{i\to f}$ contributes and we, hence, have the perturbation

$$V(\vec{r},t) = \frac{e}{2mc}\,e^{i\vec{k}\vec{r}}\vec{A}_0\cdot\vec{p}\,e^{-i\omega t} \tag{14.8}$$

$$\equiv V^+\cdot e^{-i\omega t}. \tag{14.9}$$

The transition matrix element in position basis for the H ground state reads

$$\langle f^0\,|V|\,i^0\rangle = \frac{e}{2mc}N\int d^3r\; e^{\frac{i}{\hbar}\vec{p}_f\vec{r}}\,e^{i\vec{k}\vec{r}}\vec{A}_0\,(-i\hbar\vec{\nabla})\,e^{-\frac{r}{a_0}}, \tag{14.10}$$

where the factor N consists of the normalization of a plane wave and of the H ground state, i.e.

$$N = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}}. \tag{14.11}$$

[1] $|f^0\rangle = |\vec{p}_f\rangle +$ "higher order terms in atomic potential"

Electric dipole approximation: Treating the factor $e^{i\vec{k}\vec{r}}$

The factor $e^{i\vec{k}\vec{r}}$, originating from the wave vector $\vec{k}$ of the incident electromagnetic wave, can be seen as adding the momentum $\hbar k$ to the atom in the state

$$e^{-\frac{i}{\hbar}\vec{p}_f\vec{r}}\, e^{i\vec{k}\vec{r}} = e^{-\frac{i}{\hbar}(\vec{p}_f - \vec{k}\hbar)\,\vec{r}}. \tag{14.12}$$

The multipole expansion in general is just the expansion of the exponential function, i.e.

$$e^{i\vec{k}\vec{r}} = 1 + \mathcal{O}(\vec{k}\cdot\vec{r}). \tag{14.13}$$

Now we estimate $(\vec{k}\cdot\vec{r})$ for relevant magnitudes of $\vec{k}$ an $\vec{r}$ in atomic situations.

- $|\vec{r}| \lesssim a_0$
- With $\omega = c\cdot|\vec{k}| \equiv ck$ and

  $$E_f^0 - E_i^0 = \hbar\omega, \quad E_f^0 - E_i^0 \approx 1\mathrm{Ry} = \frac{e^2}{a_0} \tag{14.14}$$

  we approximately get

  $$k = \frac{\hbar\omega}{\hbar c} \cong \frac{e^2}{\hbar c a_0}. \tag{14.15}$$

- By that we finally obtain

  $$kr \approx \frac{e^2}{\hbar c} = \alpha = \frac{1}{137} \ll 1, \tag{14.16}$$

  where α is again the fine structure constant.

The approximation

$$\boxed{e^{i\vec{k}\vec{r}} \approx 1} \tag{14.17}$$

is called *electric dipole approximation* which is very good for atomic transitions.

Physical meaning:
The wave length of an electromagnetic wave, with an amount of energy which is

relevant for atomic transitions, is much greater than the atomic radius. Therefore the electron in the atom sees a position-independent external field. If we assume a wave length of $\lambda \approx 1000$nm, one typically gets $r_{\text{Atom}} \approx 1\ \text{Å} = 10^{-1}\ nm$.

In the electric dipole approximation the $\vec{r}$-dependence of V is neglected, i.e.

$$V(t) = \frac{e}{2mc}\vec{A}_0 \cdot \vec{p}\, e^{-i\omega t} \tag{14.18}$$

$$H^0 = \frac{p^2}{2m} - \frac{e^2}{r}. \tag{14.19}$$

This perturbation is equivalent to the perturbation caused by the electric dipole momentum of the electron, $\vec{d} = -e\vec{r}$, coupling to the external electric field $\vec{E}(t) = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t}$.

$$V(t) = -\tfrac{1}{2}\vec{d} \cdot \vec{E}(\omega)\, e^{-i\omega t} \tag{14.20}$$

with

$$\vec{E}(\omega) = -\frac{i\omega}{c}\,\vec{A}_0, \tag{14.21}$$

where the prefactor 1/2 in equation (14.20) comes from geometrical considerations.

Proof:
By plugging in the commutator relation

$$[\,\vec{r}, H^0\,] = \frac{i\hbar}{m}\,\vec{p} \tag{14.22}$$

in the matrix element for any atomic transition, we get

$$\langle f^0 \,|\vec{p}|\, i^0\rangle = \frac{m}{i\hbar}\,\langle f^0 \,|(\vec{r}H^0 - H^0\vec{r})|\, i^0\rangle \tag{14.23}$$

$$= \frac{m}{i\hbar}\underbrace{(E_i^0 - E_f^0)}_{-h\bar{\omega}}\langle f^0 \,|\vec{r}|\, i^0\rangle \tag{14.24}$$

$$= im\,\omega\langle f^0 \,|\vec{r}|\, i^0\rangle \tag{14.25}$$

and therefore

$$\langle f^0 \,|\tfrac{e}{2mc}\vec{A}_0 \cdot \vec{p}|\, i^0\rangle = \langle f^0 \,|(-\tfrac{1}{2}\vec{d} \cdot \vec{E}(\omega))|\, i^0\rangle. \tag{14.26}$$

The matrix element for photo-ionization reads

$$\langle \vec{p}_f \,|V^+|\, i^0\rangle \;=\; \frac{e}{2mc}\,\frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}}\int d^3r\; e^{\frac{i}{\hbar}\vec{p}_f\vec{r}}\,\vec{A}_0\,(-i\hbar\vec{\nabla})\,e^{-\frac{r}{a_0}} \quad (14.27)$$

The integral can be evaluated by partial integration. We get the golden rule expression

$$\begin{aligned} R_{i\to f} \;&=\; \frac{2\pi}{\hbar}\left(\frac{e}{2mc}\right)^2\frac{1}{8\pi^3\hbar^3}\,\frac{1}{\pi a_0^3}\,\frac{64\pi^2 a_0^6}{[\,1+(\frac{p_f a_0}{\hbar})^2\,]^4} \\ &\quad\times|\,\vec{A}\cdot\vec{p}_f|^2\,\delta(E_f^0-E_i^0-\hbar\omega). \end{aligned} \quad (14.28)$$

- **Angular dependence of the photo-emission**

$$R_{i\to f}\sim|\vec{A}_0\cdot\vec{p}_f|^2\sim\cos^2\,(\sphericalangle(\vec{A};\vec{p}_f)), \quad (14.29)$$

which is typical for dipole characteristics. The emission, as shown in figure 14.1, occurs predominantly into the direction of the polarization of the light (as expected classically)

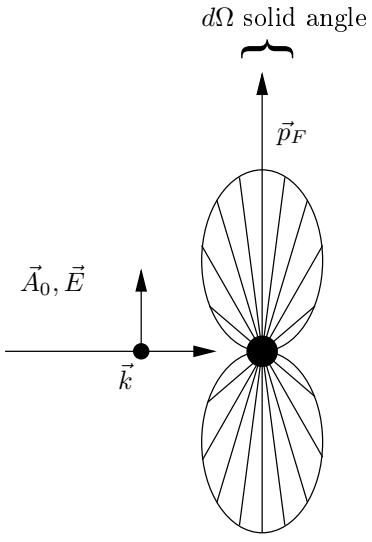

Figure 14.1: Photo-emission

- **Total photoemission rate**
  The total photoemission rate can be calculated by integrating over all momenta $\vec{p}_f$. By

$$E_f^0 = \frac{p_f^2}{2m}, \quad \partial E_f^0 = \frac{p_f}{m}\,\partial p_f \tag{14.30}$$

and

$$\delta(\tfrac{p_f^2}{2m} - E_i^0 - \hbar\omega) = \tfrac{m}{p_f}\ \delta(p_f - \sqrt{2m(E_i^0 + \hbar\omega)}) \tag{14.31}$$

one gets

$$R_{i\to\partial\Omega_f} = \frac{4a_0^3e^2}{m\pi\hbar^4c^2p_f[\,1 + (\frac{p_fa_0}{\hbar})^2\,]^4}\,|\vec{A}_0\cdot\vec{p}_f|^2\ \partial\Omega \tag{14.32}$$

with

$$p_f = \sqrt{2m(E_i^0 + \hbar\omega)}. \tag{14.33}$$

By integrating over all angles, i.e.

$$\int_0^{2\pi}\int_{-1}^{1} d\cos\theta\ \cos^2\theta = \frac{4\pi}{3}, \tag{14.34}$$

one finally obtains

$$R_{i\to\text{ion}} = \frac{16a_0^3e^2p_f}{3m\hbar^4c^2[\,1 + (\frac{p_fa_0}{\hbar})^2\,]^4}\,|\vec{A}_0|^2. \tag{14.35}$$

The photoemission rate is proportional to light intensity $|\vec{A}_0|^2$ and ionization only occurs if $\hbar\omega > -E_i^0$ (threshold) yields.

14.1.2 Absorption and stimulated emission

The dipole approximation was defined by $e^{i\vec{k}\vec{r}} \approx 1$. The time-dependent potential reads

$$\begin{aligned} V(t) &= \frac{e}{2mc}\vec{A}_0\vec{p}(e^{-i\omega t} + e^{i\omega t}) && (14.36)\\ &\equiv \widetilde{V}(e^{-i\omega t} + e^{i\omega t}), && (14.37)\end{aligned}$$

where the term proportional to $\exp(-i\omega t)$ represents absorption and the term proportional to $\exp(i\omega t)$ emission. As in section 14.1.1 we obtain for intra-atomic transitions

$$R_{i\to f} = \frac{2\pi}{\hbar}|\langle f^0|\widetilde{V}|i^0\rangle|^2\delta(E_f^0 - E_i^0 \pm \hbar\omega) \tag{14.38}$$

$$\langle f^0|\widetilde{V}|i^0\rangle = \frac{e}{2mc}\int d^3r\psi_f^{0*}(\vec{r})\vec{A}_0\cdot(-i\hbar\vec{\nabla})\psi_i^0(\vec{r}). \tag{14.39}$$

- Absorption and stimulated emission rate are proportional to the light intensity $|A_0|^2$.

- Stimulated emission of light ($E_f^0 < E_i^0$) occurs into the same wave vector $\vec{k}$ and polarization $\widehat{A}_0$ as the incident wave has (coherent emission, see field quantization).

- **Selection rules in electric dipole approximation**

$$\Delta S = 0 \quad (\text{Orthonormality of } Y_l^m\cdot\vec{\nabla}Y_l) \tag{14.40}$$

$$\Delta l = \pm 1 \tag{14.41}$$

$$\Delta m_l = \pm 1, \tag{14.42}$$

since $|f^0\rangle$ and $|i^0\rangle$ must have opposite parity. These rules are in accordance with the fact that a vector field $\vec{A}$ has spin 1!

How can spontaneous emission occur?

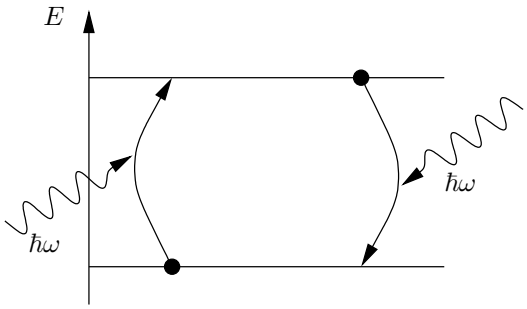

Figure 14.2: Photon absorption and emission

14.2 Field quantization and spontaneous emission

The classical treatment of the electromagnetic field (section 14.1) predicts that a transition can only occur if the amplitude of the time-dependent field $\vec{A}(t)$ is finite. In contrast, it is observed experimentally that an excited electron state decays "spontaneously", even if there is no real external field present, thereby emitting a photon.
This spontaneous decay is due to the zero-point (quantum) fluctuations of the electromagnetic field, analogous to the zero-point motion of the harmonic oscillator.
This means that even in the ground state of the electro-magnetic field there is a finite expectation value of the field intensity $\sim \langle \vec{A}^2(t) \rangle$, which induces transition of the electronic system.
In order to describe this effect, we map the dynamics of the electromagnetic field onto a harmonic oscillator problem and thereby identify its quantized eigenstates (= field quantization).
Since we had treated the harmonic oscillator in the Hamiltonian formalism, we will also seek a Hamiltonian description of the electromagnetic field dynamics here. This is not Lorentz invariant, since the Hamiltonian description treats time and space coordinates in an asymmetric way. For our present purpose, this is, however, sufficient. A more thorough treatment will be done in Quantum Mechnaics II.

14.2.1 A sketch of field quantization

In the following we will write down the Lagrangian of the free electromagnetic field, derive the Hamiltonian and show that it is equivalent to an ensemble of harmonic oscillators with eigenfrequencies $\omega = c|\vec{k}|$, where $\vec{k}$ is the wave vector of the mode.

The electromagnetic field tensor in the contravariant form is defined by

$$F^{\mu\nu} = \partial^\mu A^\nu - \partial^\nu A^\mu \tag{14.43}$$

with the explicit form

$$F^{\mu\nu} = \begin{pmatrix} 0 & E_x & E_y & E_z \\ -E_x & 0 & B_z & -B_y \\ -E_y & -B_z & 0 & B_x \\ -E_z & B_y & -B_x & 0 \end{pmatrix}, \tag{14.44}$$

where A^μ represents the components of the electromagnetic four-potential, $(A^\mu) = (\phi, \vec{A})^T$, and the electric and the magnetic field are given by

$$\vec{E} = -\tfrac{1}{c}\tfrac{\partial \vec{A}}{\partial t} - \vec{\nabla}\phi, \quad \vec{B} = \vec{\nabla} \times \vec{A}. \tag{14.45}$$

The Lagrangian of free field reads

$$\begin{aligned} L &= -\frac{1}{16\pi}\int d^3r\; F_{\mu\nu}F^{\mu\nu} && (14.46)\\ &= \frac{1}{8\pi}\int d^3r\; [\,\vec{E}^2 - \vec{B}^2\,] && (14.47)\\ &= \frac{1}{8\pi}\int d^3r\; [\,(-\tfrac{1}{c}\tfrac{\partial \vec{A}}{\partial t} - \nabla\phi)^2 - (\vec{\nabla}\times\vec{A})^2\,]. && (14.48) \end{aligned}$$

- The integration over t, i.e. the calculation of the action functional $S = \int_{t_1}^{t_2} dt\, L$, and the variation of S with respect to $\vec{A}(\vec{r},t)$ and $\phi(\vec{r},t)$ would, together with the condition $\delta S = 0$, yield the two (inhomogeneous) Maxwell equations.

- We consider free fields, i.e. $\rho = 0, \vec{j} = 0$, in the radiation gauge $\phi(\vec{r}, t) = 0$.

  Pulling the indices of the electromagnetic field tensor down, i.e. making it covariant, yields

$$F_{\mu\nu} = g_{\mu\alpha} F^{\alpha\beta} g_{\beta\nu} \tag{14.49}$$

$$(F_{\mu\nu}) = \begin{pmatrix} -1 & & & 0 \\ & 1 & & \\ & & 1 & \\ 0 & & & 1 \end{pmatrix} \begin{pmatrix} 0 & E_x & E_y & E_z \\ -E_x & 0 & B_z & -B_y \\ -E_y & -B_z & 0 & B_x \\ -E_z & B_y & -B_x & 0 \end{pmatrix} \times \begin{pmatrix} -1 & & & 0 \\ & 1 & & \\ & & 1 & \\ 0 & & & 1 \end{pmatrix} \tag{14.50}$$

$$= \begin{pmatrix} 0 & -E_x & -E_y & -E_z \\ E_x & 0 & B_z & -B_y \\ E_y & -B_z & 0 & B_x \\ E_z & B_y & -B_x & 0 \end{pmatrix} \tag{14.51}$$

$$F_{\mu\nu} F^{\mu\nu} = tr\{ (F^{\tau}_{\mu\nu}) F^{\mu\nu} \} = -2 [\vec{E}^2 - \vec{B}^2]. \tag{14.52}$$

- **Transversality conditions on the free fields**

$$\vec{\nabla} \cdot \vec{E} = 4\pi\rho = 0 \tag{14.53}$$

$$\vec{\nabla} \cdot \vec{B} = 0 \quad \Rightarrow \quad \vec{\nabla} \cdot \vec{A} = 0 \tag{14.54}$$

  Performing a Fourier transformation these conditions read

$$\vec{k} \cdot \vec{E} = 0 \tag{14.55}$$

$$\vec{k} \cdot \vec{A} = 0. \tag{14.56}$$

Hamiltonian formulation:

For convenience, we absorb the prefactor $1/8\pi$ in $\vec{A}$, i.e.

$$\widetilde{\vec{A}}(\vec{r}, t) = \frac{1}{\sqrt{8\pi}} \vec{A}(\vec{r}, t) \tag{14.57}$$

$$L = \int d^3 r \, [\underbrace{(-\tfrac{1}{c} \tfrac{\partial \widetilde{\vec{A}}}{\partial t})^2}_{T} - \underbrace{(\vec{\nabla} \times \widetilde{\vec{A}})^2}_{V}]. \tag{14.58}$$

$\widetilde{\vec{A}}(\vec{r},t) = \vec{x}$ is considered as the "elongation" analogous to the elongation $\vec{x}$ in point dynamics (at each space-time point $(\vec{r},t)$).

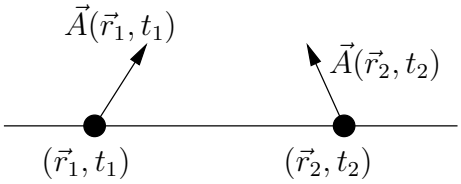

Figure 14.3: Sketch of the field $\vec{A}(\vec{r_i},t_i)$

The canonical momentum associated with $\widetilde{\vec{A}}$ reads

$$\widetilde{\vec{\Pi}}(\vec{r},t) = \frac{\partial L}{\partial \frac{\partial \widetilde{\vec{A}}}{\partial t}} = \frac{2}{c^2}\frac{\partial \widetilde{\vec{A}}}{\partial t}. \tag{14.59}$$

Notice the asymmetric treatment of $\vec{r},t$.

The Hamilton function is given by

$$H = T + V = \int d^3r\,[\,\frac{c^2}{4}\,\widetilde{\vec{\Pi}}^2 + (\vec{\nabla}\times\widetilde{\vec{A}})^2\,] \tag{14.60}$$

with

$$\begin{aligned}(\vec{\nabla}\times\widetilde{\vec{A}})\cdot(\vec{\nabla}\times\widetilde{\vec{A}}) &= \widetilde{\vec{A}}\cdot(\vec{\nabla}(\vec{\nabla}\cdot\widetilde{\vec{A}}) - \vec{\nabla}^2\widetilde{\vec{A}}) &(14.61)\\ &= -\widetilde{\vec{A}}\cdot(\vec{\nabla}^2\cdot\widetilde{\vec{A}}). &(14.62)\end{aligned}$$

Fourier transforming equation (14.60) yields

$$\widetilde{\vec{A}}(\vec{r},t) = \int \frac{d^3k}{(2\pi)^3}\,e^{i\vec{k}\vec{r}}\,\widetilde{\vec{A}}(\vec{k},t) \quad \text{etc.}, \tag{14.63}$$

so that one finally finds

$$H = \int d^3k\,[\,\tfrac{c^2}{4}\,\widetilde{\vec{\Pi}^2}(\vec{k},t) + \vec{k}^2\cdot\widetilde{\vec{A}^2}(\vec{k},t)\,]. \tag{14.64}$$

The term in brackets has the form of a (decoupled) harmonic oscillator in terms of the coordinates $\vec{x} = \widetilde{\vec{A}}$ and the momentum $\vec{p} = \widetilde{\vec{\Pi}}$ at each eigenmode $\vec{k}$ (Hamiltonian density). Because of this analogy one writes

$$H = \int d^3k\,[\,\tfrac{1}{2m}\widetilde{\vec{\Pi}^2}(\vec{k},t) + \tfrac{1}{2}m\omega^2\widetilde{\vec{A}^2}(\vec{k},t)\,] \tag{14.65}$$

with

$$\left.\begin{array}{r} m = \frac{2}{c^2} \\ \frac{1}{2}m\omega^2 = \vec{k}^2 \end{array}\right\} \omega^2 = (ck)^2, \tag{14.66}$$

which is the dispersion of electromagnetic waves.

Hence, in analogy to the harmonic oscillator (see chapter 4) we can write the elongation $\widetilde{\vec{A}}$ and the momentum $\widetilde{\vec{\Pi}}$ for each $\vec{k}$ in terms of raising/lowering operators of the excitation,

$$\begin{aligned} \widetilde{\vec{A}}(\vec{k},t) &= \sqrt{\frac{\hbar}{2m\omega}}\,(a_\lambda^\dagger + a_\lambda)\,\widehat{e}_\lambda(\vec{k}) && (14.67)\\ &= \sqrt{\frac{\hbar c}{4k}}\,(a_\lambda^\dagger(\vec{k},t) + a_\lambda(\vec{k},t))\,\widehat{e}_\lambda(\vec{k}) && (14.68)\\ \widetilde{\vec{\Pi}}(\vec{k},t) &= i\sqrt{\frac{m\hbar\omega}{2}}\,(a_\lambda^\dagger - a_\lambda)\,\widehat{e}_\lambda(\vec{k}) && (14.69)\\ &= i\sqrt{\frac{\hbar k}{c}}\,(a_\lambda^\dagger(\vec{k},t) - a_\lambda(\vec{k},t))\,\widehat{e}_\lambda(\vec{k}), && (14.70) \end{aligned}$$

where $\widehat{e}_\lambda(\vec{k})(\lambda = 1,2)$ is the transverse polarization vector which is perpendicular to $\vec{k}$ and, in addition, a unit vector. λ is called the transverse polarization. In terms of raising/lowering operators one gets

$$H = \sum_\lambda \int d^3k\ \hbar\omega\,(a^\dagger_{\vec{k},\lambda} a_{\vec{k},\lambda} + \tfrac{1}{2}) \tag{14.71}$$

with $\omega = ck$ and

$$\begin{aligned} \{\, a_\lambda(\vec{k},t),\, a^\dagger_{\lambda'}(\vec{k}',t')\,\} &= \delta_{\vec{k}\vec{k}'}\delta_{tt'}\delta_{\lambda\lambda'} && (14.72)\\ \{\, a_\lambda(\vec{k},t),\, a_{\lambda'}(\vec{k}',t')\,\} &= 0. && (14.73) \end{aligned}$$

a and $a^\dagger$ are the so-called "field operators" in $\vec{k}$-space. By

$$\begin{aligned} a(\vec{r},t) &= \int \frac{d^3k}{\sqrt{(2\pi)^3}}\, e^{i\vec{k}\vec{r}}\, a(\vec{k},t) && (14.74)\\ a^\dagger(\vec{r},t) &= \int \frac{d^3k}{\sqrt{(2\pi)^3}}\, e^{-i\vec{k}\vec{r}}\, a^\dagger(\vec{k},t) && (14.75) \end{aligned}$$

the field operators are given in position space. They represent the field quantization of the electromagnetic field. $a^\dagger_\lambda(\vec{k},t)$ creates and $a_\lambda(\vec{k},t)$ destroys a photon with wave vector $\vec{k}$ and wave length λ.

14.2.2 Spontaneous stimulated emission and decay

Using the operator structure of $\vec{A}$ derived above, we can now calculate transition matrix elements in an algebraic way.

$$\vec{A}(\vec{k},t) = \sqrt{8\pi}\,\widetilde{\vec{A}}(\vec{k},t) = \sqrt{\frac{2\pi\hbar c}{k}}\,(a^\dagger_\lambda(\vec{k},t) + a_\lambda(\vec{k},t))\,\widehat{e}_\lambda(\vec{k}) \tag{14.76}$$

$$\vec{A}(\vec{r},t) = \int \frac{d^3k}{\sqrt{(2\pi)^3}}\sqrt{\frac{2\pi\hbar c}{k}}\,(a^\dagger_\lambda(\vec{k},t)\,e^{-i\vec{k}\vec{r}} + a_\lambda(\vec{k},t)\,e^{i\vec{k}\vec{r}})\,\widehat{e}_\lambda(\vec{k}) \tag{14.77}$$

The new thing compared to the classical treatment of the electromagnetic field is that $\vec{A}$ is now an operator which changes the excitation state of the electromagnetic system, i.e. the electromagnetic system must now be considered as a part of the quantum system, and not only as an external field.

Transition rate for decay $(E^0_f < E^0_i)$**:**

$$R_{i\to f} = \frac{2\pi}{\hbar}\,|\langle f^0\,|\tfrac{e}{mc}\vec{A}\cdot\vec{p}|\,i^0\rangle|^2\delta(E^0_f - E^0_i + \hbar\omega) \tag{14.78}$$

$$|i^0\rangle = |i^0_{el}\rangle \otimes |i^0_{ph}\rangle \tag{14.79}$$

$$|f^0\rangle = |f^0_{el}\rangle \otimes |f^0_{ph}\rangle, \tag{14.80}$$

where $\vec{A}$ acts on a photonic state and $\vec{p}$ acts on an electric state.

(a) **Spontaneous decay:**
Here we consider the case that no field is applied and that the photon number vanishes, i.e. $|i^0_{ph}\rangle = |0_{ph}\rangle$.

$$\langle f^0\,|(\vec{A}\cdot\vec{p})|\,i^0\rangle = \langle f^0_{el}\,|\vec{p}|\,i^0_{el}\rangle \cdot \langle f^0_{ph}\,|\vec{A}|\,i^0_{ph}\rangle$$

$$\vec{A}(\omega) = \sum_\lambda \int \frac{d^3k}{\sqrt{(2\pi)^3}}\sqrt{\frac{2\pi\hbar c}{k}}(a^\dagger_\lambda(\vec{k}) + a_\lambda(\vec{k}))\,\widehat{e}_\lambda(\vec{k})$$

Dipole approximation:
Now we have no $\vec{r}$-dependence, so that $e^{i\vec{k}\vec{r}} = 1$.

$$\langle f^0_{ph}\,|\vec{A}(\omega)|\,0\rangle = \sum_\lambda \int \frac{d^3k}{\sqrt{(2\pi)^3}}\sqrt{\frac{2\pi\hbar c}{k}}\,\widehat{e}_\lambda(\vec{k})\,\underbrace{\langle 1_{k,\lambda}\,|a^\dagger_\lambda(\vec{k},\omega)|\,0\rangle}_{=1} \tag{14.81}$$

Therefore, in the final state we have one photon with wave vector $\vec{k}$ and wave length λ (emission). Furthermore the same rules as for the point harmonic oscillator are valid here.

- As in the classical treatment we get

$$\langle f_{el}^0 \,|\vec{p}|\, i_{el}^0 \rangle = \int d^3r \; \psi_f^{0*}(\vec{r}) \, (-i\hbar\vec{\nabla}) \, \psi_i^0(\vec{r}). \tag{14.82}$$

- Since the fluctuating electromagnetic field has components for any ω, ω is integrated over to get the total transition rate $R_{i\to f}$.

(b) **Stimulated emission:**
Here we have an applied external field with $(\omega, \vec{k}, \lambda)$ so that the initial is given by $|i_{ph}^0\rangle = |n_{k\lambda}\rangle$.

$$\langle f_{ph}^0 \,|\vec{A}(\omega)|\, i_{ph}^0 \rangle \tag{14.83}$$

$$= \sum_\lambda \int \frac{d^3k}{\sqrt{(2\pi)^3}} \sqrt{\frac{2\pi\hbar c}{k}} \, \widehat{e}_\lambda(\vec{k}) \langle (n+1)_{k,\lambda} \,|a_\lambda^\dagger(\vec{k},\omega)|\, n_{\vec{k}\lambda} \rangle \tag{14.84}$$

$$= \sum_\lambda \int \frac{d^3k}{\sqrt{(2\pi)^3}} \sqrt{\frac{2\pi\hbar c}{k}} \, \widehat{e}_\lambda(\vec{k}) \sqrt{n_{k\lambda}+1} \tag{14.85}$$

The matrix element $\langle f_{el}^0 \,|\vec{p}|\, i_{el}^0 \rangle$ is the same as for spontaneous emission.

Important consequences:
In the presence of an external electromagnetic field with (ω, k, λ) the photon is emitted in the same state, i.e. with the same momentum $\vec{k}$, polarization and phase. Therefore stimulated emission is coherent $\rightarrow$ Laser.
The stimulated emission rate $R_{i\to f}$ is enhanced compared to the spontaneous emission rate by a factor $(n_{k\lambda}+1)$, where n is the number of photons in the initial state.

14.3 Bohm-Aharonov-Effect

Figure 14.4 shows the double-slit experiment with a magnetic field.

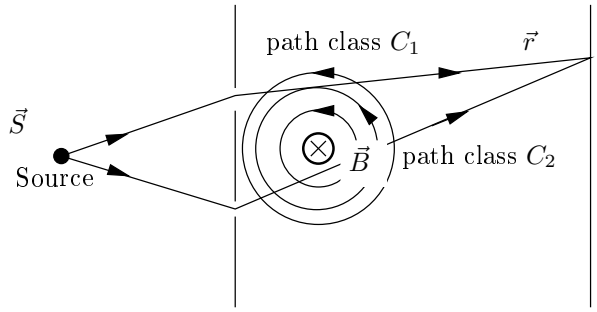

Figure 14.4: Double slit experiment with a magnetic field

The magnetic field $\vec{B}$ is confined to the region $\otimes$ perpendicular to the paper,

$$\vec{B} = \vec{\nabla} \times \vec{A}. \tag{14.86}$$

The vector potential $\vec{A}$ extends far outside, where $\vec{B} = 0$.

Gauge symmetry:
In the presence of a vector potential $\vec{A}(\vec{r})$, the wave function $\psi(r)$ acquires locally a phase,

$$\begin{aligned} \psi(\vec{r}) &= e^{-i\frac{q}{\hbar c}\Lambda(\vec{r},t)}\psi_{A=0}(\vec{r},t) && (14.87)\\ &= e^{-i\theta(\vec{r},t)}\psi_{A=0}(\vec{r},t), && (14.88) \end{aligned}$$

where $q = -e$ is the charge. We can calculate the (global) phase which a wave function acquires after the particle has traveled through a region with $\vec{A} \neq 0$ along a path C_1, C_2.

Path integral formulation:

$$\begin{aligned} \psi(\vec{r},t) &= \int d^3r'\; U(\vec{r},t;\vec{r}',t_0)\,\psi(\vec{r}',t_0) && (14.89)\\ &= U(\vec{r},t;\vec{r'},t_0)\,e^{-i\omega t_0} && (14.90) \end{aligned}$$

with a point source, i.e.

$$\psi(\vec{r}',t_0) = \delta(\vec{r}' - \vec{r}_0)\,e^{-i\omega t_0}. \tag{14.91}$$

The propagator is given by

$$U(\vec{r},t;\vec{s},t_0) = \sum_{\text{paths}} e^{-\frac{i}{\hbar}S}\cdot N, \tag{14.92}$$

where N is a normalization factor. The action functional consists of a part containing a free particle and another part describing a vector field $\vec{A}$, i.e.

$$S = \int_{t_0}^{t} dt' \ (\tfrac{1}{2} m \dot{\vec{r}}^2 - \tfrac{q}{c} \dot{\vec{r}} \cdot \vec{A}(\vec{r})) + \mathcal{O}(\vec{A}^2). \tag{14.93}$$

Gauge transformation:
The wave function, the vector potential and the action functional are transformed as follows. $\frac{q}{\hbar c} \Lambda(\vec{r}, t)$ represents the phase factor.

$$\begin{aligned}
\psi(\vec{r}) &\longrightarrow e^{-i \frac{q}{\hbar c} \Lambda(\vec{r}, t)} && (14.94)\\
\vec{A}(\vec{r}) &\longrightarrow \vec{A}_\Lambda(\vec{r}) = \vec{A}(\vec{r}) - \vec{\nabla} \Lambda(\vec{r}, t) && (14.95)\\
S \longrightarrow S_\Lambda &= S - \int_{t_0}^{t} dt' \ \tfrac{q}{c} (\dot{\vec{r}}' \cdot \vec{\nabla} \Lambda \left(\vec{r}', t'\right) + \tfrac{\partial \Lambda}{\partial t'}) && (14.96)\\
&= S - \int_{t_0}^{t} dt' \ \tfrac{q}{c} (\tfrac{\partial \Lambda(\vec{r}', t')}{\partial t'}) && (14.97)\\
&= S - \tfrac{q}{c} (\Lambda(\vec{r}, t) - \Lambda(\vec{r}_0, t_0)) && (14.98)
\end{aligned}$$

The phase factor for each path C due to the magnetic field $\vec{B}$ reads

$$e^{\frac{iq}{\hbar c} \int_{t_0}^{t} dt' \ (\vec{v} \cdot \vec{A})} = e^{\frac{iq}{\hbar c} \int_{\vec{r}_0}^{\vec{r}} d\vec{r}' \cdot \vec{A}}. \tag{14.99}$$

Here we have used that $\vec{A}$ is a constant in time and we have substituted

$$d\vec{r}' = \frac{d\vec{r}}{d\vec{t}'} \, dt'. \tag{14.100}$$

Two different paths C_1, C_2 only differ by the phase

$$\begin{aligned}
\Delta\theta &= \frac{q}{\hbar c} \int_{\substack{\vec{r}_0 \\ c_1}}^{\vec{r}} dr' \cdot \vec{A} - \frac{q}{\hbar c} \int_{\substack{\vec{r}_0 \\ c_2}}^{\vec{r}} dr' \cdot \vec{A} && (14.101)\\
&= \frac{q}{\hbar c} \oint dr' \cdot \vec{A} = \frac{q}{\hbar c} \int d\vec{S} \cdot \underbrace{\vec{\nabla} \times \vec{A}}_{\vec{B}} && (14.102)\\
&= \frac{q}{\hbar c} \phi = \frac{\phi}{\phi_0} 2\pi && (14.103)
\end{aligned}$$

The flux ϕ is enclosed by c_1, c_2 and furthermore the factor $\phi_0 = \frac{2\pi\hbar c}{q} = \frac{hc}{q}$ is the so-called flux quantum.

- A phase difference only occurs if there is a real magnetic flux enclosed.

- Hence, the phase difference is a global effect:
  Two paths must enclose a finite area in order to acquire a finite phase difference.

Therefore a classical particle traverses only a single path, i.e. is not sensitive to $\vec{A}$. A quantum mechanical particle probes all paths and the path classes 1 or 2 have all the same phase.

The total wave function on the screen is given by

$$\psi(\vec{r}) = \sum_{\substack{\text{Path} \\ \text{class } C_1}} e^{\frac{iq}{\hbar c}\int_{c_1} d\vec{r}'\cdot\vec{A}}\,\psi_1(\vec{r}) + \sum_{\substack{\text{Path} \\ \text{class } C_2}} e^{\frac{iq}{\hbar c}\int_{c_2} d\vec{r}'\cdot\vec{A}}\,\psi_2(\vec{r}) \tag{14.104}$$

$$= \alpha\,[\,\psi_1(\vec{r}) + e^{i2\pi\frac{\phi}{\phi_0}}\,\psi_2(\vec{r})\,]. \tag{14.105}$$

This can be interpreted as a shift of the interference pattern.

Chapter 15

Non-perturbative Approximation Methods

General remarks:

- *Perturbation theory:*
  - Small parameter (perturbation) necessary for expansion
  - Systematical: Well-defined prescription of how to calculate effects of a perturbation up to a given order
- *Nonperturbative methods:*
  For problems where the perturbation is large or where the system is unstable.
  - No small parameter necessary
  - Not systematical: Knowledge about the solution must be put into the method

15.1 Variational method (Ritz' variation principle)

The Ritz variation principle is a method for finding the approximate ground state energy and the ground state wave function.

(1.) Choose a *model wave function* $|\psi\rangle = |\psi\rangle_{a_1 \ldots a_n}$ which depends on one or several parameters. This defines a subset of Hilbert space (not necessarily

space), in which the approximate solution is to be found.

$$\{\, |\psi\rangle_{a_1 \ldots a_n} | a_i \, \epsilon M_i, \quad i = 1, ..., n\} = U \tag{15.1}$$

(2.) Minimize the expectation value of the Hamiltonian in the subset U with respect to $a_1 ... a_n$, i.e.

$$\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \tag{15.2}$$

should become minimal. This method gives an *upper bound* for the *ground state energy* and an approximate ground state wave function. The accuracy of this method depends on the proper choice of the model wave function.

Example: Helium atom

$$H = \left(\frac{-\hbar^2 \vec{\nabla}_1^2}{2m} - \frac{Ze^2}{\vec{x}_1} \right) + \left(\frac{-\hbar^2 \vec{\nabla}_2^2}{2m} - \frac{Ze^2}{\vec{x}_2} \right) + \frac{e^2}{|\vec{x}_1 - \vec{x}_2|}, \tag{15.3}$$

where $Z = 2$ is the nuclear charge number and $\vec{x}_1, \vec{x}_2$ are the coordinates of the electrons respectively. We expect that both electrons are in an s-wave state (Para-Helium). The effect of the second electron on the motion of the first electron is approximately to screen the nuclear charge.

Model wave function:
The Slater determinant of two H ground state wave functions according to an effective nuclear charge $\bar{Z}$ is given by

$$\psi(\vec{x}_1, \vec{x}_2, \bar{Z}) = \psi_0(\vec{x}_1, \bar{Z})\, \psi_0(\vec{x}_2, \bar{Z})\, \tfrac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right). \tag{15.4}$$

Furthermore the normalized hydrogen ground state wave function reads

$$\psi_0(\vec{x}, \bar{Z}) = \sqrt{\frac{1}{\pi \bar{a}_0^3}}\, e^{-\frac{r}{\bar{a}_0}} \tag{15.5}$$

with

$$\bar{a}_0 = \frac{\hbar^2}{\bar{Z} m e^2}. \tag{15.6}$$

Energy expectation value:

$$\begin{aligned}
\langle H\rangle_{\bar{Z}} &= \langle\psi|H|\psi\rangle_{\bar{Z}} && (15.7)\\
&= 2\,E_0(\bar{Z}) - 2\,\langle\psi_0|\tfrac{e^2(Z-\bar{Z})}{r}|\psi_0\rangle + \langle\psi|\tfrac{e^2}{|\vec{x}_1-\vec{x}_2|}|\psi\rangle && (15.8)\\
E_0(\bar{Z}) &= -\tfrac{m\bar{Z}^2e^4}{2\hbar^2} = -\bar{Z}^2Ry && (15.9)\\
\langle\psi_0|\tfrac{e^2\bar{Z}}{r}\,\tfrac{Z-\bar{Z}}{\bar{Z}}|\psi_0\rangle &= 2\,Ry\bar{Z}^2\,\tfrac{Z-\bar{Z}}{\bar{Z}} && (15.10)\\
\langle\psi|\tfrac{e^2}{|x_1-x_2|}|\psi\rangle &= \frac{5}{4}\,\bar{Z}Ry && (15.11)\\
\langle H\rangle_{\bar{Z}} &= 2\,Ry\,(-\bar{Z}^2 - 2\bar{Z}(Z-\bar{Z}) + \tfrac{5}{8}\bar{Z}) && (15.12)\\
&= 2\,Ry\,(\bar{Z}^2 - 2\bar{Z}Z + \tfrac{5}{8}\bar{Z}) && (15.13)
\end{aligned}$$

Minimum for the effective reduced charge:

$$\begin{aligned}
\frac{\partial}{\partial\bar{Z}}\langle H\rangle_Z &= 2\,Ry\,(2\bar{Z} - 2Z + \frac{5}{8}) = 0 && (15.14)\\
\bar{Z} &= Z - \frac{5}{16} = 2 - \frac{5}{16} = \frac{27}{16}, && (15.15)
\end{aligned}$$

since Z is in this case 2.

15.2 The method of the self-consistent field (Hartree and Hartree-Fock method)

In this section we want to discuss an approximation method for systems of several or many particles. The direct product wave function

$$\psi = \varphi_1(\vec{x}_1)\varphi_2(\vec{x}_2)...\varphi_N(\vec{x}_N) \tag{15.16}$$

or Slater determinant is an exact solution only if the Hamiltonian is a sum of single-particle Hamiltonians, i.e. for systems without particle-particle interaction.
In the Hartree and in the Hartree-Fock approximations the particle-particle interaction is treated approximately and one assumes that the problem of a single particle in an arbitrary external potential is solvable.

- **Hartree approximation:**
  The many-particle wave function is *approximated* by a direct product of single-particle wave functions. For one given particle, let's say particle i, the density of the other $(N-1)$ particles generates an effective potential and one determines all N single-particle wave functions for this problem $\rightarrow$ self-consistent problem.

- **Hartree-Fock approximation:**
  In addition to the Hartree approximation, the total antisymmetry of the wave function is taken into account, i.e. a Slater determinant of single-particle wave functions is taken as an Ansatz.

Hartree approximation:
We will derive the Hartree approximation from variational principle. First of all we define the many-particle wave function as a product of single-particle wave functions,

$$\psi(\vec{x}_1, ..., \vec{x}_N) = \varphi_1(1)...\varphi_N(2), \tag{15.17}$$

where the single-particle wave functions are given by

$$\varphi_i(i) = \varphi_i(\vec{x}_i)\,\chi(m_{s_i}). \tag{15.18}$$

$\varphi_i(\vec{x}_i)$ is the position wave function and $\chi(m_{s_i})$ is the spin wave function. The normalization condition, which will be implemented by Lagrange parameters ε_i, reads

$$\int d^3x\ |\varphi_i(\vec{x})|^2 = 1, \quad i = 1, ..., N. \tag{15.19}$$

$$\langle H\rangle - \sum_i \varepsilon_i \left(\int d^3x\ \varphi_i^*(\vec{x})\,\varphi_i(\vec{x}) - 1 \right) = \tag{15.20}$$

$$\sum_i \left\{ \int d^3x\ [\,\varphi_i^*(\vec{x})\,(-\tfrac{\hbar^2}{2m}\vec{\nabla}^2 - \tfrac{Ze^2}{|\vec{x}|} - \varepsilon_i)\,\varphi_i(\vec{x})\,] + \varepsilon_i \right\}$$

$$+ \sum_{i\neq j} \int d^3x \int d^3y\ \varphi_i^*(\vec{x})\,\varphi_j^*(\vec{y})\,\tfrac{e^2}{|\vec{x}-\vec{y}|}\,\varphi_i(\vec{x})\,\varphi_j(\vec{y}) \tag{15.21}$$

The variation with respect to $\varphi_i^*(\vec{x})$ yields

$$\left(-\tfrac{\hbar^2}{2m}\vec{\nabla}^2 - \tfrac{Ze^2}{|\vec{x}|} + \textstyle\sum_{j\neq i}\int d^3y\ \tfrac{e^2|\varphi_j(\vec{y})|^2}{|\vec{x}-\vec{y}|}\right)\varphi_i(\vec{x}) = \varepsilon_i\,\varphi_i, \tag{15.22}$$

where the factor $e^2|\varphi_j(\vec{y})|^2/|\vec{x}-\vec{y}|$ is the charge density $\rho(y)$ of particles $j \neq i$. Equation (15.22) is the single-particle Schrödinger equation for a particle i in an effective potential generated by the external potential and by the charge density of the particles $j \neq i$. The Lagrange parameter ε_i is the single-particle eigenenergy.

Hartree-Fock approximation: (fermions)

Ansatz:

$$\psi(1,...,N) = \begin{vmatrix} \varphi_1(1) & \cdots & \varphi_1(N) \\ \vdots & & \vdots \\ \varphi_N(1) & \cdots & \varphi_N(N) \end{vmatrix} \tag{15.23}$$

Expectation value of H in the Slater state ψ:

$$\langle H\rangle - \sum_i \varepsilon_i \left(\int d^3x\, \varphi_i^*(\vec{x})\, \varphi_i(\vec{x}) - 1 \right) \tag{15.24}$$

$$= \sum_i \left\{ \int d^3x\, [\varphi_i^*(\vec{x})(-\tfrac{\hbar^2}{2m}\vec{\nabla}^2 - \tfrac{Ze^2}{|\vec{x}|} - \varepsilon_i)\, \varphi_i(\vec{x})] + \varepsilon_i \right\} \tag{15.25}$$

$$+\frac{1}{2}\sum_{i\neq j} \int d^3x \int d^3y\, \varphi_i^*(\vec{x})\, \varphi_j^*(\vec{y}) \frac{e^2}{|\vec{x}-\vec{y}|} \varphi_j(\vec{y})\, \varphi_i(\vec{x}) \tag{15.26}$$

$$-\frac{1}{2}\sum_{i\neq j} \int d^3x \int d^3y\, \varphi_i^*(\vec{x})\, \varphi_j^*(\vec{y}) \frac{e^2}{|\vec{x}-\vec{y}|}\, \varphi_j(\vec{x})\, \varphi_i(\vec{y})\, \delta_{m_{si},m_{sj}} \tag{15.27}$$

$$\tag{15.28}$$

Variation with respect to $\varphi_i^*(\vec{x})$:

$$\begin{aligned} &(-\tfrac{\hbar^2}{2m}\vec{\nabla}^2 - \tfrac{Ze^2}{|\vec{x}|})\, \varphi_i(\vec{x}) + \textstyle\sum_{i\neq j} \int d^3y\, \frac{e^2}{|\vec{x}-\vec{y}|} |\varphi_j(\vec{y})|^2\, \varphi_i(\vec{x}) \\ &-\frac{1}{2}\sum_{i\neq j} \delta_{m_{si},m_{sj}} \int d^3y\, \frac{e^2}{|\vec{x}-\vec{y}|}\, \varphi_j^*(\vec{y})\, \varphi_i(\vec{y})\, \varphi_j(\vec{x}) \end{aligned} \tag{15.29}$$

$$= \varepsilon_i\, \varphi_i(\vec{x}) \tag{15.30}$$

Remarks:

- The Hartree and the Hartree-Fock equations are a set of *self-consistent, non-linear integro-differential* equations.

- They can be derived from a variational principle. This means that, at least for the ground state, the H- or HF approximations give the best single-particle direct product of Slater wave functions.