

Quantenmechanik I

Skript zur Vorlesung von
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am

Physik-Institut
der
Universität Zürich

im

Herbstsemester 2022

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This script is based on Manfred Sigrist's lecture notes: I thank him for letting me use the L^AT_EXsource code. The notes were then translated, revised and further developed by Maurizio Storni: a big thank you to him too.

Chapter 1

The early quantum mechanics

At the end of the 19th century, the physical worldview was based on what we now call “classical physics”: the essential pillars were classical mechanics (Newton), electrodynamics (Maxwell), and thermodynamics (Boltzmann). This conception was challenged at the beginning of the 20th century by a series of experiments: essential were examples such as the spectral distribution of electromagnetic radiation, the photo-emission of electrons from metals, and discrete atomic spectra. An expansion of the worldview seemed inevitable and then led to a fundamental revolution of the physical worldview during the first 30 years of the 20th century. In this chapter, we will give a brief overview of the most important early events and discoveries.

1.1 The Planck radiation law (1900)

We consider electromagnetic radiation in a cube-shaped cavity with perfectly reflecting (i.e., ideally conducting) walls with sidelength L in thermodynamic equilibrium with temperature T . Using the methods of classical electrodynamics, i.e. solving the wave equation taking into account boundary conditions, one can calculate the number of modes (natural oscillations) in the frequency interval $[\omega, \omega + d\omega]$:

$$N(\omega) = \frac{L^3}{\pi^2 c^3} \omega^2, \quad (1.1)$$

where c is the speed of light. Thus, the corresponding energy density $u(\omega, T)$ of electromagnetic radiation (energy per volume in the frequency interval $[\omega, \omega + d\omega]$) is

$$u(\omega, T) = \frac{\bar{\varepsilon}(\omega, T)}{\pi^2 c^3} \omega^2, \quad (1.2)$$

where $\bar{\varepsilon}(\omega, T)$ is the mean energy of the mode with frequency ω at temperature T .

In classical electrodynamics, the energy of the modes depends on the amplitude of the oscillations and can take continuous (non-quantized) values: the law of equal distribution then provides that in thermodynamic equilibrium each mode has the mean energy $\bar{\varepsilon}(\omega, T) = k_B T$, with k_B the Boltzmann constant, independent of frequency. From this follows immediately the Rayleigh-Jeans law:

$$u(\omega, T) = \frac{k_B T}{\pi^2 c^3} \omega^2. \quad (1.3)$$

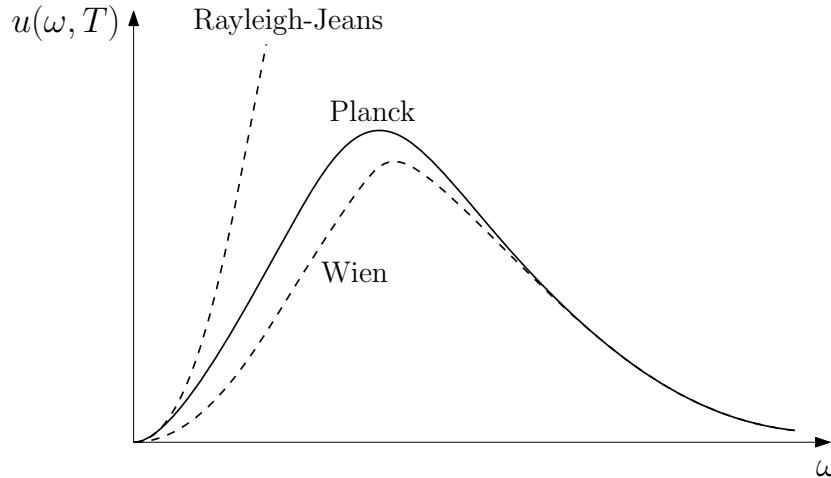


Figure 1.1: Energy density of the electromagnetic radiation in a cavity: the Planck, Wien, and Rayleigh-Jeans radiation laws in comparison.

For small frequencies ($\omega \rightarrow 0$) this formula reproduces well the measured behavior, but for large frequencies ($\omega \rightarrow \infty$) it diverges, the so-called “ultraviolet catastrophe”, in contradiction with the empirical asymptotic behavior (Wien, 1896),

$$u(\omega, T) \propto \omega^3 e^{-C\frac{\omega}{T}}, \quad \omega \rightarrow \infty, \quad (1.4)$$

(from the behavior for $\omega \rightarrow \infty$ of Planck's radiation law (1.6) one can see that the constant C has the value \hbar/k_B , with \hbar the reduced Planck constant).

Planck derived in his seminal work the interpolation between the two limiting cases (Fig. 1.1), the Planck's radiation law, by assuming that the radiation is absorbed and emitted by the walls in energy quanta $\hbar\omega$. It follows that the energy of the modes is not continuously distributed, but can take only discrete values $E_n = n\hbar\omega$, with n the integer occupation number of the mode with frequency ω . The mean energy of the modes can then be determined with the Boltzmann distribution,

$$\bar{\varepsilon}(\omega, T) = \frac{\sum_{n=0}^{\infty} E_n e^{-\frac{E_n}{k_B T}}}{\sum_{n=0}^{\infty} e^{-\frac{E_n}{k_B T}}} = \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1}, \quad (1.5)$$

and gives Planck's radiation law:

$$u(\omega, T) = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1}. \quad (1.6)$$

This law perfectly reproduced the experimental data and, in addition, Planck was able to determine some of the constants with very good accuracy, as shown in the following table.

Constant	Planck	today
\hbar	$1.04 \cdot 10^{-34} \text{ Js}$	$1.05457 \cdot 10^{-34} \text{ Js}$
k_B	$1.34 \cdot 10^{-23} \text{ J/K}$	$1.3807 \cdot 10^{-23} \text{ J/K}$
$N_A = R/k_B$	$6.17 \cdot 10^{23} \text{ Mol}^{-1}$	$6.022 \cdot 10^{23} \text{ Mol}^{-1}$

1.2 Light as a particle: photoelectric effect (1905) and Compton scattering (1922)

Electromagnetic radiation hitting a metal surface can cause the emission of electrons, the so-called photoemission. In the classical approach, one would expect the energy of the emitted electrons to be determined by the intensity of the radiation, which enters the material as an electromagnetic wave and accelerates the electrons. In reality, however, the electron energy depends on the frequency ω of the radiation, while the intensity determines the number of emitted electrons (Lenard, 1902).

Conversely, electrons emit electromagnetic radiation when they abruptly lose energy, as in “bremsstrahlung” experiments, where electrons from the cathode release X-rays when they hit the anode.

The light quantum hypothesis of Einstein (1905) solved the puzzle. Einstein assumed that monochromatic light of frequency ω transfers its energy to the electrons in quanta $\hbar\omega$, one quantum per electron. For the kinetic energy of the outgoing electrons we get

$$E_e = \frac{1}{2}m_e v^2 = \hbar\omega - W, \quad (1.7)$$

where m_e is the mass and v the velocity of the electron; W is the work function, i.e. the energy necessary to free an electron from the metal. It results that the kinetic energy depends linearly on the frequency of the light (with proportionality constant \hbar) and that only light with frequency greater than $\omega_0 = W/\hbar$ can cause photoemission: the light quanta with smaller frequency do not have enough energy (Fig. 1.2). The light intensity is proportional to the number of incident light quanta

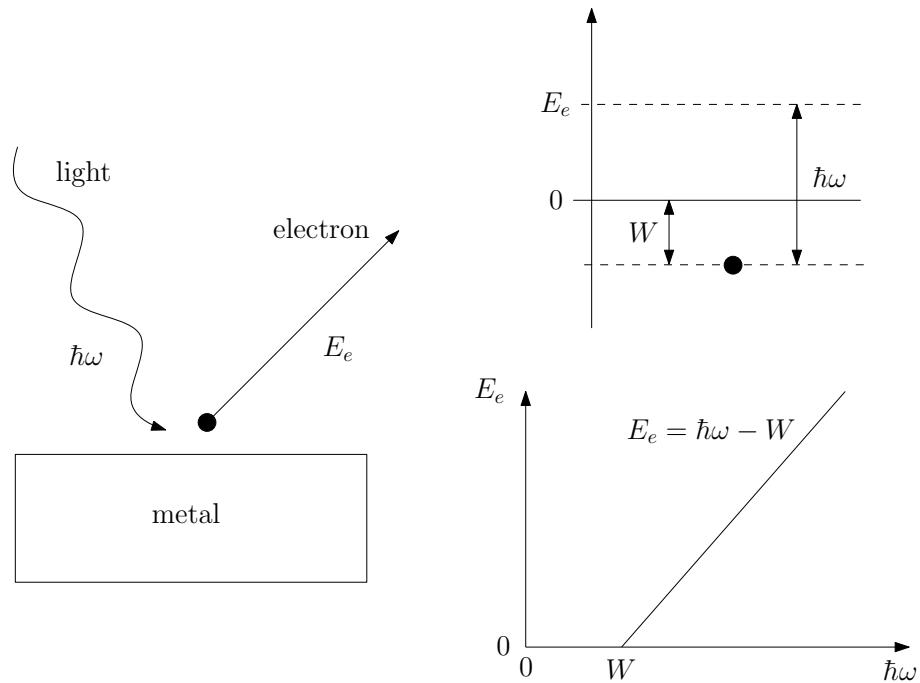


Figure 1.2: The photoelectric effect.

and thus affects only the number of electrons released when $\omega > \omega_0$.

Furthermore, Einstein showed that Wien's radiation law (1.4) can be interpreted to mean that monochromatic radiation in a cavity behaves like an ideal gas of independent particles whose energy is $E = \hbar\omega$.

This actually laid the foundation for the particle-wave duality of light, in which light in interaction with matter has particle character: light consists of massless particles, *photons*, which propagate at the speed of light. Each photon of monochromatic radiation with frequency ω (and wavelength λ) has energy

$$E = \hbar\omega \quad (1.8)$$

and momentum

$$\mathbf{p} = \hbar\mathbf{k}, \quad (1.9)$$

where \mathbf{k} is the wave vector with $|\mathbf{k}| = \omega/c = 2\pi/\lambda$. From $\omega = 2\pi c/\lambda$ follows that, for photons, energy is proportional to momentum:

$$E = |\mathbf{p}|c. \quad (1.10)$$

The particle character of light appears clearly in the so-called Compton scattering (1922): high energy photons (γ -radiation) hitting electrons perform a collision like particles, so that the energy and the momentum of the photons are changed. This implies that the frequency and wavelength of the photons are different before and after the collision.

We consider a photon with wave vector \mathbf{k} (and wavelength λ) colliding with an electron at rest; after the collision let \mathbf{k}' be the wave vector for the photon (λ' its wavelength) and \mathbf{p}' the momentum for the electron (Fig. 1.3). Four-momentum conservation then implies:

$$\begin{pmatrix} E_{\text{tot}}/c \\ \mathbf{p}_{\text{tot}} \end{pmatrix} = \underbrace{\begin{pmatrix} \hbar|\mathbf{k}| \\ \hbar\mathbf{k} \end{pmatrix}}_{\text{before the collision}} + \underbrace{\begin{pmatrix} m_e c \\ 0 \end{pmatrix}}_{\text{after the collision}} = \underbrace{\begin{pmatrix} \hbar|\mathbf{k}'| \\ \hbar\mathbf{k}' \end{pmatrix}}_{\text{before the collision}} + \underbrace{\begin{pmatrix} \sqrt{|\mathbf{p}'|^2 + m_e^2 c^2} \\ \mathbf{p}' \end{pmatrix}}_{\text{after the collision}}, \quad (1.11)$$

with $E = \sqrt{|\mathbf{p}|^2 c^2 + m^2 c^4}$, the relativistic relation between energy and momentum. Elimination of the electron momentum gives the wavelength shift for the light:

$$\lambda' - \lambda = 4\pi\lambda_C \sin^2 \frac{\theta}{2}, \quad (1.12)$$

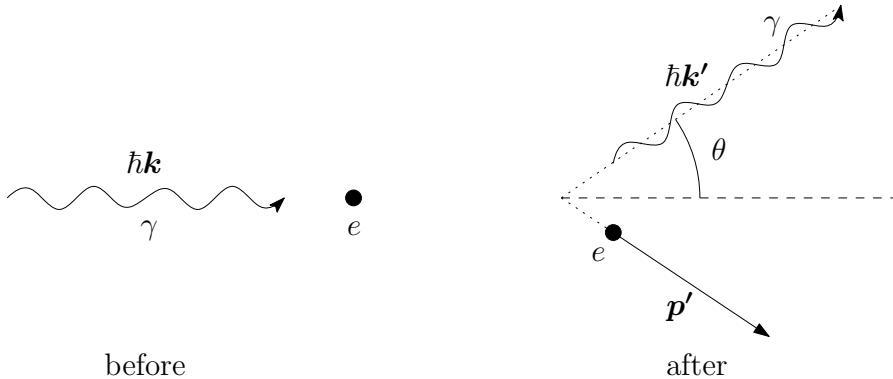


Figure 1.3: Compton scattering.

where

$$\lambda_C = \frac{\hbar}{m_e c} \quad (1.13)$$

is the Compton wavelength. It results that the wavelength of the scattered photon depends on the scattering angle θ .

1.3 Atomic spectra: the atomic model of Bohr (1913)

Atoms exhibit discrete light emission spectra. For the hydrogen atom (H atom), the empirically derived formula for the emitted frequencies applies (Balmer, 1885),

$$\omega_{nm} = C \left(\frac{1}{m^2} - \frac{1}{n^2} \right), \quad (1.14)$$

where n and m are positive integers with $n > m$. Since light is absorbed or emitted by electrons in quanta $\hbar\omega$, the Balmer formula corresponds to a discrete energy spectrum of the H atom:

$$E_n = -\frac{\text{Ry}}{n^2}, \quad (1.15)$$

with the Rydberg constant $\text{Ry} = \hbar C \approx 13.6 \text{ eV}$.

Bohr, who tackled this problem in 1913, relied on the Rutherford model of this atom, which assumes a positively charged nucleus around which a negatively charged electron orbits. The classical orbit of an electron in the attractive electrostatic field of the nucleus lies in a plane. Bohr assumed a circular orbit described by the equation of motion

$$m_e r \omega^2 = \frac{e^2}{r^2}, \quad (1.16)$$

where r is the orbit radius, ω die angular frequency (angular speed) and e the elementary charge. The angular momentum, perpendicular to the orbital plane, is

$$L = m_e r^2 \omega. \quad (1.17)$$

For a charged particle such an orbit is not stable, since it would quickly lose its energy and crash into the nucleus due to the centripetal acceleration continuously emitting radiation. Bohr's "way out" was the *postulate* that the electrons can take only quantized values for the angular momentum,

$$L_n = \hbar n, \quad n = 1, 2, 3, \dots, \quad (1.18)$$

where $n = 1$ indicates the smallest possible quantum. This ad hoc stability condition solved the problem for the hydrogen-like atoms in a surprisingly consistent manner. The total energy of the electron on its orbit is

$$E = E_{\text{kin}} + E_{\text{pot}} = \frac{L^2}{2m_e r^2} - \frac{e^2}{r}. \quad (1.19)$$

Together with equation of motion (1.16) and angular momentum (1.17) we get

$$r = \frac{L^2}{m_e e^2} \quad (1.20)$$

and

$$E = -\frac{m_e e^4}{2L^2}. \quad (1.21)$$

The quantization condition (1.18) then leads to the orbit radius

$$r_n = a_0 n^2 \quad (1.22)$$

with the Bohr radius

$$a_0 = \frac{\hbar^2}{m_e e^2} = 0.529 \cdot 10^{-10} \text{ m} \quad (1.23)$$

and to the energy

$$E_n = -\frac{\text{Ry}}{n^2} \quad (1.24)$$

with the Rydberg constant

$$\text{Ry} = \frac{m_e e^4}{2\hbar^2} = 13.6 \text{ eV.} \quad (1.25)$$

In this way, not only the spectrum for the H-atom and the He⁺-ion was quantitatively correct, but also the orbital radii had magnitudes comparable to empirical values for the dimensions of the atoms.

The Balmer formula then results from the fact that the electron can jump between the differently quantized orbits under emission or absorption of a photon. For example, at the transition from the quantum number n to the quantum number m (for $n > m$) a photon with energy

$$\hbar\omega_{nm} = E_n - E_m = \text{Ry} \left(\frac{1}{m^2} - \frac{1}{n^2} \right) \quad (1.26)$$

is emitted. The change of the energy of the electron takes place only with the absorption or emission of exactly determined photon energy quanta.

Furthermore Bohr demanded that for large quantum numbers n the classical radiation theory is reproduced: at the transition $n \rightarrow n - 1$ light with frequency equal to the classical orbital frequency of the electron should be emitted:

$$\omega_{\text{classical}} = \frac{L_n}{m_e r_n^2} = \frac{2\text{Ry}}{\hbar n^3}. \quad (1.27)$$

For $n \gg 1$ the spectrum becomes quasi-continuous and the transition between next orbits gives the following frequency for emitted photons:

$$\omega_{n,n-1} = \frac{\text{Ry}}{\hbar} \left(\frac{1}{(n-1)^2} - \frac{1}{n^2} \right) \approx \frac{2\text{Ry}}{\hbar n^3}, \quad (1.28)$$

in correspondence with (1.27). This connection with classical physics was generally formulated by Bohr in 1923 as the so-called *correspondence principle*: “The quantum theory reproduces classical physics in the limiting case of large quantum numbers.”

We shall encounter other formulations later.

1.4 The Bohr-Sommerfeld quantization (1915)

The Bohr quantization of angular momentum was generalized by Sommerfeld for periodic particle orbits. Here the action variable I of classical mechanics plays an important role. For a one-dimensional system it is defined as

$$I = \frac{1}{2\pi} \oint p dq, \quad (1.29)$$

where \oint is the integral over a closed classical orbit in phase space with energy E . Here p is the momentum conjugate to the coordinate q . In classical mechanics I together with the angular variable W forms a pair of canonical coordinates with

$$\dot{I} = 0 \quad \text{and} \quad \dot{W} = \frac{dE(I)}{dI} = \text{const.}, \quad (1.30)$$

where the energy of the system E depends only on I . It follows that I is a conserved quantity and that W grows linearly by 2π at each pass and thus corresponds to a frequency $\omega_{\text{classical}} = \dot{W} = \frac{dE(I)}{dI}$.

The Bohr-Sommerfeld quantization is defined by a condition for the action variable I definiert:

$$I_n = \frac{1}{2\pi} \oint p dq = \hbar(n + \alpha), \quad n \text{ integer.} \quad (1.31)$$

The Planck constant \hbar obviously has the unit of action $[I] = \text{J}\cdot\text{s}$. The possible values of the integer quantum number n are restricted by those that the action on the left-hand side can take at all. The constant α cannot be fixed by any simple principle, but remains within this theory an empirical quantity and depends essentially on the details of the physics at the reversal points of the classical orbits.

One can simply see that for the H atom this quantization condition is compatible with the correspondence principle,

$$\omega_{n,n-1} = \frac{E_n - E_{n-1}}{\hbar} = \frac{E_n - E_{n-1}}{I_n - I_{n-1}} \xrightarrow{n \rightarrow \infty} \frac{dE(I)}{dI} = \dot{W} = \omega_{\text{classical}}. \quad (1.32)$$

This means that the frequency of electromagnetic radiation emitted at high quantum numbers corresponds to the frequency of the classical motion. The quantization of the action can be applied to other systems with periodic orbits, such as the harmonic oscillator, and gives correct values for the quantization of the energy.

The Bohr-Sommerfeld quantization can also be applied to several *separable* canonical variables (p_i, q_i) , which then individually satisfy the condition,

$$I_{i,n} = \frac{1}{2\pi} \oint p_i dq_i = \hbar(n_i + \alpha_i). \quad (1.33)$$

The multiplicity of quantum numbers now also allows the discussion of the degeneracy of energy levels, i.e. the determination of the number of different electron orbits with the same energy. Furthermore this extension also allows to discuss selection rules for transition in atoms.

In the hydrogen atom we find three independent variables, and consequently three quantum numbers, which are related to the radial and the azimuthal motion in the orbital plane and the orientation of the orbital plane. The calculation leads to a degeneracy of the energy E_n of n^2 , i.e. there are n^2 orbits (*states*) with the same energy E_n . The lowest energy E_1 , the *ground state*, is not degenerate¹.

While the quantization of the energy levels for closed orbits of bound particles has been very well reproduced by this recipe, the lacking of an answer to the deeper question about the “why” was very unsatisfactory. Furthermore, the quantum aspects of important problems such as particle scattering could not be treated in this form. A new and more advanced concept was needed.

1.5 Particle-wave duality: the de Broglie wavelength (1923)

Light behaves both as a wave and as a particle, and it depends on the circumstances, which approach should be used to interpret physical processes. De Broglie dared in 1923 the bold step to postulate the same for electrons. The four-vector of the electron with energy E and momentum \mathbf{p} is considered as

$$\begin{pmatrix} E/c \\ \mathbf{p} \end{pmatrix} = \hbar \begin{pmatrix} \omega/c \\ \mathbf{k} \end{pmatrix}, \quad (1.34)$$

analogous to the photon. The electron behaves like a wave with frequency ω and wave vector \mathbf{k} . Thus the electron has a wavelength λ defined by its momentum or its energy,

$$\lambda = \frac{2\pi\hbar}{|\mathbf{p}|} = \frac{2\pi\hbar}{\sqrt{2m_e E}} = \frac{12.2\text{\AA}}{\sqrt{E(\text{eV})}}, \quad (1.35)$$

where, non-relativistically, $E = |\mathbf{p}|^2/2m_e$. Since electronvolt (eV) is the typical energy scale for electrons, the typical wavelength is in the range of Angström (Å). The wave nature of the electron should be clearly evident in phenomena which take place on comparable lengthscales, like in an atom or in scattering phenomena of electrons in crystal lattices with lattice constant $\sim 5\text{\AA}$ (Davisson-Germer experiment, 1927).

The double-slit experiment in optics is a prime example for the consideration of particle-wave duality. Light and electrons show qualitatively the same interference pattern. The intensity on the screen is proportional to the square of the sum of the amplitudes A_1 and A_2 of the two beams through slit 1 and 2, respectively,

$$I \propto |A_1 + A_2|^2. \quad (1.36)$$

Since these are waves, both contributions carry a phase, so that

$$|A_1 + A_2|^2 = |A_1|^2 + |A_2|^2 + (A_1^* A_2 + A_1 A_2^*) \neq |A_1|^2 + |A_2|^2, \quad (1.37)$$

¹Spin degeneracy is not considered here

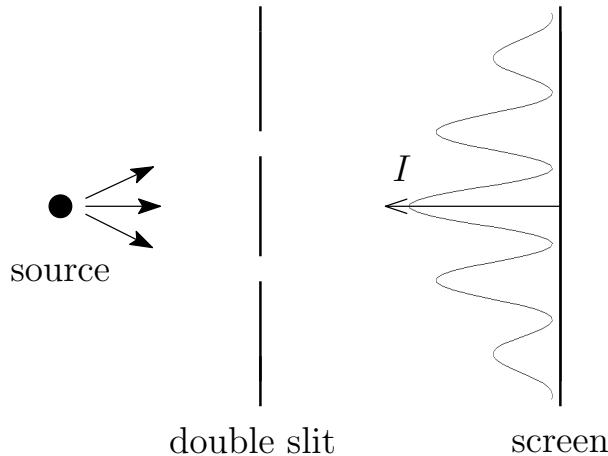


Figure 1.4: Particle-wave duality: double-slit experiment.

i.e., the intensity for the double-slit experiment is not the sum of the intensities of each open slit $I_i \propto |A_i|^2$: the two rays interfere. The interference pattern that results is the realization of the wave nature of the light and of the electron. However, on the screen (photoplate) not the waves, but individual particles, photons or electrons, are responsible for the local reaction. The interference not an effect, which is caused by the large number of particles, but exists for each particle separately. The interference pattern is then the result of statistics, which determines where the particles (electrons or photons) hit with larger or smaller probability.

The de Broglie's idea of particle-wave duality was the starting point for *wave mechanics* as formulated by Schrödinger in 1926. Almost at the same time (1925) also the *matrix mechanics* was developed by Heisenberg. Both formulations are equivalent and indeed, together with the so-called *Copenhagen interpretation* (1927), give a certain understanding and a complete theory of quantum physics. While Heisenberg's matrix mechanics has shaped the language and interpretation of quantum mechanics, Schrödinger's wave mechanics has proved to be a computationally more practical formulation for considering many concrete problems.

1.6 Heisenberg's uncertainty principle (1927)

In Heisenberg's matrix mechanics the conjugate variables momentum p and coordinate q appear as "operators" which do not commute with each other. As we will see, this has the consequence that both quantities cannot be determined exactly at the same time. For the mean deviations Δp and Δq of the two quantities, the uncertainty relation holds:

$$\Delta p \cdot \Delta q \geq \frac{\hbar}{2}. \quad (1.38)$$

For independent variables (in a separable system), i.e. for operators which commute, there is no such restriction.

The uncertainty relation (1.38) means that, in contrast to classical mechanics, where the future (or past) of a particle is completely (deterministically) determined

by the specification of the present momentum and location, such a determination is no longer possible. The classical determinism is replaced by a new quantum mechanical determinism.

An important consequence of the uncertainty of localized particle trajectories is that there is a so-called zero-point motion: the momentum of a particle increases the more one tries to fix its position and, of course, vice versa. Applied to the one-dimensional harmonic oscillator (with mass m and frequency ω) we come to the following conclusion for the lowest (most localized) particle state. The energy is given by

$$E = \frac{p^2}{2m} + \frac{m\omega^2}{2}q^2 \geq \frac{p^2}{2m} + \frac{m\omega^2}{2}\frac{\hbar^2}{4p^2}. \quad (1.39)$$

where $p = \Delta p$ and $q = \Delta q$ are considered as deviations around the equilibrium point $q = p = 0$ and thus $q \geq \frac{\hbar}{2p}$. We can minimize the last expression with respect to p and then obtain

$$E \geq \frac{\hbar\omega}{2}, \quad (1.40)$$

which corresponds to a lower bound for the energy larger than $E = 0$, the classically lowest energy. It is this uncertainty relation that also “stabilizes” the hydrogen atom, since the electron cannot fall into the nucleus without driving its momentum (and kinetic energy) towards infinity.

Other interesting conjugate variables with an uncertainty relation are energy E and time t , because, using the example of a free particle,

$$\Delta E = \Delta \left(\frac{p^2}{2m} \right) = \frac{\langle p \rangle}{m} \Delta p \quad (1.41)$$

and

$$\Delta t = \Delta \left(\frac{q}{v} \right) = \frac{m}{\langle p \rangle} \Delta q, \quad (1.42)$$

where $\langle p \rangle$ is the average momentum of the particle. It follows that

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}, \quad (1.43)$$

a relation which should be interpreted in words as follows: the longer a particle remains in a state of certain energy, the more exactly one can determine this energy. This is reflected for example in spectral lines which have a frequency width (corresponding to an energy uncertainty ΔE). We will see later that this uncertainty is related to the lifetime or decay time of the state. The longer a state lives the sharper its spectral line appears.

These are the basic concepts on which we now want to mathematically build the modern quantum mechanics.

Chapter 2

Schrödinger's quantum mechanics

2.1 Wave function and Schrödinger equation for a free particle

The particle-wave duality suggests that the behavior of a particle in a volume V (analogous to the electromagnetic wave) can be described by a complex wave function $\psi(\mathbf{r}, t)$. On the one hand, $\psi(\mathbf{r}, t)$ should follow the superposition principle followed by waves, on the other hand it should include the concept of probability if we want to observe the particle locally in a detector. The interpretation of the magnitude square of the wave function,

$$|\psi(\mathbf{r}, t)|^2 d^3r \quad (2.1)$$

corresponds to the probability to find the particle at time t in the infinitesimal space-volume element d^3r around the position \mathbf{r} . I.e. $|\psi(\mathbf{r}, t)|^2$ is a *probability density* and one calls $\psi(\mathbf{r}, t)$ a *probability amplitude*. Obviously, the wave function should belong to the space $L^2(V)$ of the square-integrable functions and *at all times t satisfy the condition*

$$\int_V d^3r |\psi(\mathbf{r}, t)|^2 = 1, \quad (2.2)$$

i.e. the probability of finding the particle anywhere in the volume V is 1. We call this the *normalization* of ψ .

We note that $L^2(V)$ is a vector space and thus the *superposition principle* is realized in a *natural way*: for *every two normalized wave functions* $\psi_1(\mathbf{r}, t)$ and $\psi_2(\mathbf{r}, t)$ in $L^2(V)$, their linear combination $\psi(\mathbf{r}, t) = c_1\psi_1(\mathbf{r}, t) + c_2\psi_2(\mathbf{r}, t)$ is also an allowed wave function in $L^2(V)$, where the (complex) *coefficients c_1 and c_2 must be chosen such that the resulting wave function $\psi(\mathbf{r}, t)$ is also normalized*. The probability density for $\psi(\mathbf{r}, t)$ is then

$$|\psi(\mathbf{r}, t)|^2 = |c_1\psi_1(\mathbf{r}, t) + c_2\psi_2(\mathbf{r}, t)|^2, \quad (2.3)$$

i.e. just as in the double-slit experiment, the amplitudes are first added and then squared. The result is generally not equal to the sum of the individual squares $|c_1\psi_1(\mathbf{r}, t)|^2 + |c_2\psi_2(\mathbf{r}, t)|^2$: interference effects occur.

The time evolution of the wave function is determined by a differential equation which was found by Schrödinger in 1926 at UZH and satisfies the following conditions:

1. $\psi(\mathbf{r}, t)$ depends only on one initial condition, the wave function $\psi(\mathbf{r}, 0)$ at $t = 0$.
 \Rightarrow First order differential equation in time
2. Superposition principle for $\psi(\mathbf{r}, t)$, i.e., with the solutions $\psi_1(\mathbf{r}, t)$ and $\psi_2(\mathbf{r}, t)$ is also the linear combination $c_1\psi_1(\mathbf{r}, t) + c_2\psi_2(\mathbf{r}, t)$ a solution.
 \Rightarrow Differential equal is linear in $\psi(\mathbf{r}, t)$
3. $\psi(\mathbf{r}, t) \in L^2(V)$ and remains normalizable for all t .
 \Rightarrow Differential equation is homogeneous
4. For a free particle with mass m and momentum \mathbf{p} the wave function should have the form of a plane wave (à la de Broglie).
 \Rightarrow For a free particle with momentum \mathbf{p} the function

$$\psi(\mathbf{r}, t) = A \exp\left[\frac{i}{\hbar} (\mathbf{p} \cdot \mathbf{r} - E_{\mathbf{p}} t)\right] \quad (2.4)$$

should be a solution, with $E_{\mathbf{p}} = \mathbf{p}^2/2m$ the particle energy and A a normalization constant

The differential equation for a free particle that satisfies these conditions has the form

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}, t), \quad (2.5)$$

and is called *Schrödinger equation* (∇^2 is the Laplace operator). Inserting the plane wave

$$\psi(\mathbf{r}, t) = A e^{\frac{i}{\hbar} (\mathbf{p} \cdot \mathbf{r} - E_{\mathbf{p}} t)} \quad (2.6)$$

one finds that it is indeed a solution.

Obviously, this wave function cannot be normalized in infinite space, because $|\psi(\mathbf{r}, t)|^2 = |A|^2$ is a constant. It is usual to reduce the domain of ψ to a finite cubic domain with edge length L . This requires boundary conditions, which we assume to be periodic (in the limiting case $L \rightarrow \infty$ the choice of the boundary conditions will not matter), i.e.,

$$\psi(\mathbf{r}, t) = \psi(\mathbf{r} + (L, 0, 0), t) = \psi(\mathbf{r} + (0, L, 0), t) = \psi(\mathbf{r} + (0, 0, L), t). \quad (2.7)$$

These give the condition

$$\mathbf{p} = (p_x, p_y, p_z) = \frac{2\pi\hbar}{L} (n_x, n_y, n_z) \quad \text{wobei} \quad n_x, n_y, n_z = 0, \pm 1, \pm 2, \dots, \quad (2.8)$$

which corresponds to a quantization of the particle states¹, a general phenomenon when forcing a particle in a finite volume. Thus, for the normalization of ψ we get: $A = 1/\sqrt{V}$ with $V = L^3$.

¹This quantization can of course be understood again within the Bohr-Sommerfeld quantization because of the periodicity, where we have three separable canonical variables.

2.1. WAVE FUNCTION AND SCHRÖDINGER EQUATION FOR A FREE PARTICLE

We note that the plane wave (2.6) describes a particle with sharp momentum \mathbf{p} , i.e. $\Delta\mathbf{p} = 0$, but because $|\psi(\mathbf{r}, t)|^2$ is constant, it provides no information about the particle's position, i.e. $\Delta\mathbf{r} \rightarrow \infty$, in agreement with Heisenberg's uncertainty principle. To describe a localized particle, i.e., with $\Delta\mathbf{r} < \infty$, we need a wave function with $\Delta\mathbf{p} > 0$: a superposition of many plane waves. Such a wave function is called a *wave packet*²,

$$\psi(\mathbf{r}, t) = \int \frac{d^3 p}{(2\pi\hbar)^3} \tilde{\psi}(\mathbf{p}, t) e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}} = \int \frac{d^3 p}{(2\pi\hbar)^3} \tilde{\psi}(\mathbf{p}, 0) e^{\frac{i}{\hbar} (\mathbf{p} \cdot \mathbf{r} - E_{\mathbf{p}} t)}. \quad (2.9)$$

This is the general form of a wave function of a free particle and because of the superposition principle it is also a solution of the Schrödinger equation (2.5). Note that the first equal sign corresponds to an (inverse) Fourier transform and thus the amplitude $\tilde{\psi}(\mathbf{p}, t) = \tilde{\psi}(\mathbf{p}, 0) e^{-\frac{i}{\hbar} E_{\mathbf{p}} t}$ can be represented with the transformation:

$$\tilde{\psi}(\mathbf{p}, t) = \int d^3 r \psi(\mathbf{r}, t) e^{-\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}}. \quad (2.10)$$

According to Parseval's theorem,

$$\int \frac{d^3 p}{(2\pi\hbar)^3} |\tilde{\psi}(\mathbf{p}, t)|^2 = \int d^3 r |\psi(\mathbf{r}, t)|^2 = 1, \quad (2.11)$$

i.e. $\tilde{\psi}(\mathbf{p}, t)$ is also normalized at all times and like a wave function it leads to the probability distribution in momentum space, i.e.

$$|\tilde{\psi}(\mathbf{p}, t)|^2 \frac{d^3 p}{(2\pi\hbar)^3} \quad (2.12)$$

is the probability at time t to find the particle within the momentum space volume element $d^3 p / (2\pi\hbar)^3$ around the momentum \mathbf{p} .

With the help of the wave functions it is possible to calculate expectation values (mean values) of measurable quantities. The expectation value of the position (of the momentum) can be determined particularly simply in the spatial representation (momentum space representation):

$$\begin{aligned} \text{position: } \langle \mathbf{r} \rangle &= \int d^3 r \mathbf{r} |\psi(\mathbf{r}, t)|^2, \\ \text{momentum: } \langle \mathbf{p} \rangle &= \int \frac{d^3 p}{(2\pi\hbar)^3} \mathbf{p} |\tilde{\psi}(\mathbf{p}, t)|^2. \end{aligned} \quad (2.13)$$

²The integrals in momentum space are for the limiting case $L \rightarrow \infty$ and extend over the whole \mathbb{R}^3 , as do the integrals in position space. In the case of finite volume, the integrals in momentum space are to be replaced by sums over all allowed vectors \mathbf{p} in (2.8); the integrals in position space extend correspondingly only over the volume V .

But it also applies

$$\begin{aligned}
 & \int d^3r \psi^*(\mathbf{r}, t) \frac{\hbar}{i} \nabla_{\mathbf{r}} \psi(\mathbf{r}, t) = \\
 &= \int \frac{d^3p_1}{(2\pi\hbar)^3} \int \frac{d^3p_2}{(2\pi\hbar)^3} \tilde{\psi}^*(\mathbf{p}_1, t) \tilde{\psi}(\mathbf{p}_2, t) \underbrace{\int d^3r e^{-\frac{i}{\hbar}\mathbf{p}_1 \cdot \mathbf{r}} \frac{\hbar}{i} \nabla_{\mathbf{r}} e^{\frac{i}{\hbar}\mathbf{p}_2 \cdot \mathbf{r}}}_{\mathbf{p}_2(2\pi\hbar)^3 \delta^{(3)}(\mathbf{p}_2 - \mathbf{p}_1)} \\
 &= \int \frac{d^3p_2}{(2\pi\hbar)^3} \mathbf{p}_2 |\tilde{\psi}(\mathbf{p}_2, t)|^2 = \langle \mathbf{p} \rangle,
 \end{aligned} \tag{2.14}$$

where equation (2.9) was used and the properties of the δ distributions were used³. From the above calculation it follows that the momentum \mathbf{p} in the spatial representation has the form $\frac{\hbar}{i} \nabla_{\mathbf{r}}$:

$$\mathbf{p} \leftrightarrow \frac{\hbar}{i} \nabla_{\mathbf{r}}. \tag{2.15}$$

Conversely, the position \mathbf{r} in the momentum representation has a differential form,

$$\mathbf{r} \leftrightarrow -\frac{\hbar}{i} \nabla_{\mathbf{p}}. \tag{2.16}$$

We consider now the expectation value of the kinetic energy,

$$\langle E \rangle = \left\langle \frac{\mathbf{p}^2}{2m} \right\rangle = \int \frac{d^3p}{(2\pi\hbar)^3} \frac{\mathbf{p}^2}{2m} |\tilde{\psi}(\mathbf{p}, t)|^2 \tag{2.17}$$

$$= \int d^3r \psi^*(\mathbf{r}, t) \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 \right) \psi(\mathbf{r}, t). \tag{2.18}$$

Note that $\langle E \rangle$ is time independent, since $\tilde{\psi}(\mathbf{p}, t) = \tilde{\psi}(\mathbf{p}, 0) e^{-\frac{i}{\hbar} E_{\mathbf{p}} t}$ and thus $|\tilde{\psi}(\mathbf{p}, t)|^2 = |\tilde{\psi}(\mathbf{p}, 0)|^2$, which is a consequence of the conservation of energy. We can express $\langle E \rangle$ also as

$$\langle E \rangle = \int d^3r \psi^*(\mathbf{r}, t) i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t), \tag{2.19}$$

since

$$\begin{aligned}
 & \int d^3r \psi^*(\mathbf{r}, t) i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \\
 &= \int \frac{d^3p_1}{(2\pi\hbar)^3} \frac{d^3p_2}{(2\pi\hbar)^3} \tilde{\psi}^*(\mathbf{p}_1, 0) \tilde{\psi}(\mathbf{p}_2, 0) \underbrace{\int d^3r e^{-\frac{i}{\hbar}(\mathbf{p}_1 \cdot \mathbf{r} - E_{\mathbf{p}_1} t)} i\hbar \frac{\partial}{\partial t} e^{\frac{i}{\hbar}(\mathbf{p}_2 \cdot \mathbf{r} - E_{\mathbf{p}_2} t)}}_{E_{\mathbf{p}_2}(2\pi\hbar)^3 \delta^{(3)}(\mathbf{p}_2 - \mathbf{p}_1)} \\
 &= \int \frac{d^3p_2}{(2\pi\hbar)^3} E_{\mathbf{p}_2} |\tilde{\psi}(\mathbf{p}_2, t)|^2 = \langle E \rangle.
 \end{aligned} \tag{2.20}$$

The energy E can thus also be represented as a time differential:

$$E \leftrightarrow i\hbar \frac{\partial}{\partial t}. \tag{2.21}$$

³For a summary of the properties of the δ distributions, see appendix A.

For a free particle the kinetic energy $E_{\mathbf{p}} = \mathbf{p}^2/2m$ corresponds to the Hamiltonian function $H(\mathbf{p})$. Therefore, the Schrödinger equation for a free particle (2.5) can be written as follows,

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = H \left(\frac{\hbar}{i} \nabla_{\mathbf{r}} \right) \psi(\mathbf{r}, t), \quad (2.22)$$

where $H(\mathbf{p}) \rightarrow H(\hbar \nabla_{\mathbf{r}}/i)$. Thus the Hamilton function describes the evolution (propagation) of the wave function in time. We will use this remark later to formulate the Schrödinger equation for a particle in a potential.

2.2 Propagation of the wave function for a free particle

The time evolution of the wave function $\tilde{\psi}(\mathbf{p}, t)$ in momentum space is determined by the time-dependent phase factor $\exp(-iE_{\mathbf{p}}t/\hbar)$ and is for a free particle in the momentum representation particularly simple,

$$\tilde{\psi}(\mathbf{p}, t) = e^{-\frac{i}{\hbar} E_{\mathbf{p}}(t-t')} \tilde{\psi}(\mathbf{p}, t'). \quad (2.23)$$

As already noted, the probability density in momentum space is then constant in time: $|\tilde{\psi}(\mathbf{p}, t)|^2 = |\tilde{\psi}(\mathbf{p}, 0)|^2$.

Let us now study the time evolution in the position representation. If we insert (2.23) in (2.9) and use (2.10), we find:

$$\psi(\mathbf{r}, t) = \int d^3 r' K(\mathbf{r} - \mathbf{r}', t - t') \psi(\mathbf{r}', t'), \quad (2.24)$$

with the *propagator*

$$K(\mathbf{r} - \mathbf{r}', t - t') = \int \frac{d^3 p}{(2\pi\hbar)^3} e^{\frac{i}{\hbar} (\mathbf{p} \cdot (\mathbf{r} - \mathbf{r}') - E_{\mathbf{p}}(t - t'))}. \quad (2.25)$$

This integration is similar to the Fourier transform of a Gaussian function⁴, since $E_{\mathbf{p}} = \mathbf{p}^2/2m$, and the result is

$$K(\mathbf{r} - \mathbf{r}', t - t') = \left(\frac{m}{2\pi i\hbar(t - t')} \right)^{3/2} \exp \left(\frac{im(\mathbf{r} - \mathbf{r}')^2}{2\hbar(t - t')} \right). \quad (2.27)$$

We now want to calculate the time evolution of a Gaussian wave packet. A particle can be understood as a propagating wave packet with a certain spatial

⁴The one-dimensional Fourier transform of a Gaussian function is

$$\int_{\mathbb{R}} dx e^{-ax^2} e^{ikx} = \sqrt{\frac{\pi}{a}} e^{-\frac{k^2}{4a}}. \quad (2.26)$$

Using methods of complex analysis, one can show that this equation is also valid for $a \in \mathbb{C}$ with $\operatorname{Re}(a) \geq 0$. (In the limiting case $\operatorname{Re}(a) \rightarrow 0$ one speaks of Fresnel integrals).

extension. We study here a particle moving in one-dimensional space and consider the situation in which the (normalized) wave packet has the Gaussian form at $t = 0$,

$$\psi(x, 0) = \frac{1}{(2\pi D)^{1/4}} e^{\frac{i\hbar p_0 x}{\hbar}} e^{-\frac{(x-x_0)^2}{4D}}, \quad (2.28)$$

where x_0 describes the mean position and \sqrt{D} the spatial width of the packet. We will see in a moment that p_0 is the mean momentum of the wave packet; the wave function in the momentum representation at $t = 0$ also has a Gaussian form,

$$\begin{aligned} \tilde{\psi}(\hbar k, 0) &= \int dx \psi(x, 0) e^{-ikx} \\ &= \frac{1}{(2\pi D)^{1/4}} \int dx e^{-\frac{(x-x_0)^2}{4D}} e^{-i(k-k_0)x} \\ &= \frac{1}{(2\pi D)^{1/4}} e^{-i(k-k_0)x_0} \int dy e^{-\frac{y^2}{4D}} e^{-i(k-k_0)y} \\ &= (8\pi D)^{1/4} e^{-i(k-k_0)x_0} e^{-D(k-k_0)^2}, \end{aligned} \quad (2.29)$$

centered around $p_0 = \hbar k_0$ (where we use the wave vector $k = p/\hbar$ instead of the momentum, performed the substitution $y = x - x_0$ and used equation (2.26)).

The propagation of this wave packet is now obtained by superposition of plane waves as above,

$$\begin{aligned} \psi(x, t) &= \int \frac{dk}{2\pi} \tilde{\psi}(\hbar k, 0) e^{i(kx - \frac{\hbar k^2}{2m}t)} \\ &= (8\pi D)^{1/4} \int \frac{dk}{2\pi} e^{-i(k-k_0)x_0} e^{-D(k-k_0)^2} e^{i(kx - \frac{\hbar k^2}{2m}t)} \\ &= (8\pi D)^{1/4} e^{ik_0 x} e^{-\frac{i\hbar k_0^2 t}{2m}} \int \frac{dq}{2\pi} e^{iq(x - \frac{\hbar k_0}{m}t - x_0)} e^{-\frac{i\hbar q^2 t}{2m}} e^{-Dq^2} \\ &= \left(\frac{D}{2\pi D_t^2} \right)^{1/4} e^{ik_0 x} e^{-\frac{i\hbar k_0^2 t}{2m}} e^{-\frac{(x-v_0 t - x_0)^2}{4D_t}}, \end{aligned} \quad (2.30)$$

with the substitution $q = k - k_0$ and the Fourier transform of the Gaussian function (2.26). Furthermore, in the last line, $v_0 = \hbar k_0/m$ and $D_t = D + i\hbar t/2m$.

With this wave function we can now calculate the time dependence of the expectation values of different measurable quantities. We note first that the probability density in the position representation,

$$|\psi(x, t)|^2 = \left(\frac{D}{2\pi|D_t|^2} \right)^{1/2} e^{-\frac{(x-v_0 t - x_0)^2}{4} \left(\frac{1}{D_t} + \frac{1}{D_{t^*}} \right)} \quad (2.31)$$

$$= \left(\frac{D}{2\pi|D_t|^2} \right)^{1/2} e^{-D \frac{(x-v_0 t - x_0)^2}{2|D_t|^2}}, \quad (2.32)$$

is a Gaussian distribution. From it we find the average position of the particle (mean value),

$$\langle x \rangle = \int dx x |\psi(x, t)|^2 = x_0 + v_0 t \quad (2.33)$$

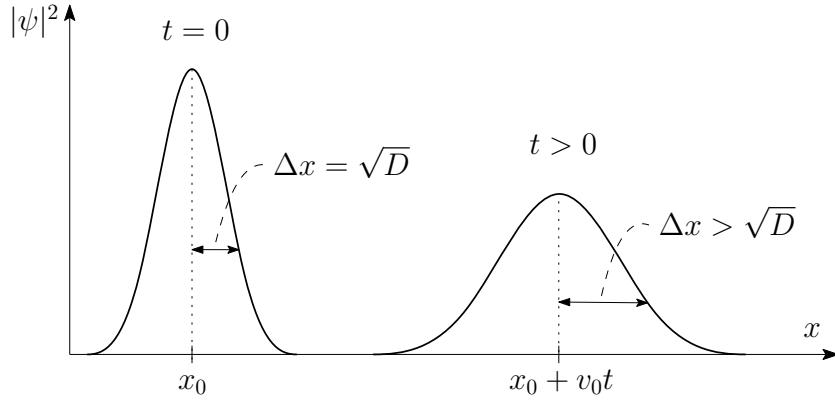


Figure 2.1: Delocalization of a wave packet.

and the **squared mean deviation** (variance),

$$(\Delta x)^2 = \langle (x - \langle x \rangle)^2 \rangle = \frac{|D_t|^2}{D} = D \left(1 + \frac{\hbar^2 t^2}{4m^2 D^2} \right). \quad (2.34)$$

Analogously, in the **momentum representation**,

$$|\tilde{\psi}(\hbar k, t)|^2 = (8\pi D)^{1/2} e^{-2D(k-k_0)^2}, \quad (2.35)$$

From which we get the **average momentum**,

$$\langle p \rangle = \int \frac{dk}{2\pi} \hbar k |\tilde{\psi}(\hbar k, t)|^2 = \hbar k_0 = p_0, \quad (2.36)$$

and the corresponding squared mean deviation,

$$(\Delta p)^2 = \langle (p - \langle p \rangle)^2 \rangle = \frac{\hbar^2}{4D}. \quad (2.37)$$

We can interpret these expectation values as follows: The **mean value** and **the deviation of the momentum** are constant in time, as expected from conservation of momentum and energy ($E \propto p^2$). The mean position of the wave packet follows the classical trajectory of a free particle, $x_0 + v_0 t$, with v_0 the **mean velocity** (group velocity): $\frac{1}{\hbar} \frac{dE_k}{dk}|_{k=k_0} = v_0$. But at the same time we notice a “delocalization” of the wave packet: its width increases with time, i.e. the position of the particle becomes less localized (see Fig. 2.1). For $t \rightarrow \infty$ we get $\Delta x \propto t$.

If we consider Heisenberg’s uncertainty principle,

$$\Delta x \cdot \Delta p = \frac{\hbar}{2} \sqrt{1 + \left(\frac{\hbar t}{2mD} \right)^2} \geq \frac{\hbar}{2}, \quad (2.38)$$

we find that the **minimum uncertainty** $\hbar/2$ is assumed at $t = 0$ and then increases with time.

The delocalization of the Gaussian wave packet is similar to the diffusion of particles (e.g. in Brownian motion). Note, however, that for $t \rightarrow \infty$,

$$\begin{aligned}\Delta x_{\text{QM}} &\propto t \\ \Delta x_{\text{diffusion}} &\propto t^{1/2}.\end{aligned}\tag{2.39}$$

The probability distribution of the classical diffusion delocalizes slower for long times.

2.3 Schrödinger equation with potential

The correspondence principle can now be reformulated. We introduce the following mappings between classical variables and new quantum mechanical operators. If we consider the formulation in the position representation, then the following relations hold:

$$\mathbf{r} \rightarrow \hat{\mathbf{r}} = \mathbf{r} \quad \mathbf{p} \rightarrow \hat{\mathbf{p}} = \frac{\hbar}{i} \nabla \quad E \rightarrow i\hbar \frac{\partial}{\partial t}.\tag{2.40}$$

In this way, the variables become operators acting on the wave function. As noted at the end of section 2.1, the Hamiltonian describes the evolution of the wave function in time. The general Schrödinger equation is now obtained from the classical Hamilton function by substituting these operators for the variables.

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = H(\hat{\mathbf{p}}, \hat{\mathbf{r}}, t) \psi(\mathbf{r}, t)\tag{2.41}$$

where $H(\hat{\mathbf{p}}, \hat{\mathbf{r}}, t)$ is obtained from the classical Hamilton function,

$$H(\mathbf{p}, \mathbf{r}, t) \rightarrow \hat{H} = H\left(\frac{\hbar}{i} \nabla, \mathbf{r}, t\right).\tag{2.42}$$

This means that the classical Hamilton function H becomes the Hamilton operator \hat{H} . This leads then to the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \hat{H} \psi(\mathbf{r}, t).\tag{2.43}$$

For a particle in an external potential $V(\mathbf{r})$ the Schrödinger equation is then

$$H(\mathbf{p}, \mathbf{r}) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \rightarrow i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}, t).\tag{2.44}$$

For a charged particle (with charge q) in an electromagnetic field we get

? why

$$\begin{aligned}H(\mathbf{p}, \mathbf{r}) &= \frac{1}{2m} \left(\mathbf{p} - \frac{q}{c} \mathbf{A}(\mathbf{r}) \right)^2 + q\phi(\mathbf{r}) \\ \rightarrow i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) &= \left[\frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{q}{c} \mathbf{A}(\mathbf{r}) \right)^2 + q\phi(\mathbf{r}) \right] \psi(\mathbf{r}, t),\end{aligned}\tag{2.45}$$

where ϕ and \mathbf{A} are the electromagnetic potentials. From this principle results the connection of quantum mechanics with classical mechanics.

It is now also clear how to formulate the quantum mechanics for a system with N particles. We introduce a wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; t)$ which satisfies the following Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; t) = \hat{H}(\hat{\mathbf{p}}_1, \dots, \hat{\mathbf{p}}_N; \hat{\mathbf{r}}_1, \dots, \hat{\mathbf{r}}_N) \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; t), \quad (2.46)$$

which in the general case leads to a very complex mathematical problem. We postpone the discussion of the many-particle problem to later chapters.

2.4 Postulates of quantum mechanics

From the correspondence principle we can now derive the Schrödinger equation for a quantum mechanical system and in this way describe the dynamics of the wave function. In summary, Schrödinger's quantum theory is based on the following postulates in the position space formulation:

P1: The state of a system is described by the wave function $\psi(\mathbf{r}, t)$, and the quantity $|\psi(\mathbf{r}, t)|^2 d^D r$ corresponds to the probability to find the particle at time t at the position \mathbf{r} within the volume element $d^D r$, where D is the space dimension.

P2: Measurable quantities (observables) of classical physics correspond to quantum mechanical operators, and the expectation value of the observable is defined as

$$\langle \hat{A} \rangle = \int d^D r \psi^*(\mathbf{r}, t) \hat{A} \psi(\mathbf{r}, t). \quad (2.47)$$

P3: The time evolution of the wave function is determined by the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \hat{H} \psi(\mathbf{r}, t), \quad (2.48)$$

where \hat{H} is the Hamilton operator.

An analogous formulation is also possible in the momentum space representation.

2.5 Probability current and continuity equation

As we postulated above, $|\psi(\mathbf{r}, t)|^2$ has the interpretation of a probability density

$$\rho(\mathbf{r}, t) = |\psi(\mathbf{r}, t)|^2. \quad (2.49)$$

The Schrödinger equation for a particle in a potential (2.44),

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}, t), \quad (2.50)$$

and its complex conjugate,

$$-i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t)^* = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}, t)^*, \quad (2.51)$$

determine the time evolution of this probability density:

$$\begin{aligned} \frac{\partial}{\partial t} \rho(\mathbf{r}, t) &= \psi(\mathbf{r}, t)^* \frac{\partial}{\partial t} \psi(\mathbf{r}, t) + \psi(\mathbf{r}, t) \frac{\partial}{\partial t} \psi(\mathbf{r}, t)^* \\ &= \frac{i\hbar}{2m} [\psi(\mathbf{r}, t)^* \nabla^2 \psi(\mathbf{r}, t) - \psi(\mathbf{r}, t) \nabla^2 \psi(\mathbf{r}, t)^*] \end{aligned} \quad (2.52)$$

$$-\frac{i}{\hbar} [\psi(\mathbf{r}, t)^* V(\mathbf{r}) \psi(\mathbf{r}, t) - \psi(\mathbf{r}, t) V(\mathbf{r}) \psi(\mathbf{r}, t)^*]. \quad (2.53)$$

The last line vanishes and we find the continuity equation

$$\frac{\partial}{\partial t} \rho(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0, \quad (2.54)$$

with the probability current density

$$\mathbf{j}(\mathbf{r}, t) = \frac{\hbar}{2mi} [\psi(\mathbf{r}, t)^* \nabla \psi(\mathbf{r}, t) - \psi(\mathbf{r}, t) \nabla \psi(\mathbf{r}, t)^*]. \quad (2.55)$$

Thus, probability behaves like an incompressible fluid (or like electric charge): it can neither be annihilated nor generated; it can change in a volume V only by flowing out of it or flowing into it:

$$\frac{\partial}{\partial t} \int_V d^3 r |\psi(\mathbf{r}, t)|^2 = - \int_{\partial V} d\mathbf{S} \cdot \mathbf{j}(\mathbf{r}, t). \quad (2.56)$$

It follows, in particular, that the normalization of the wave function is time independent: if we take for V the total volume of the system, then the time derivative of the normalization is on the left-hand side. The flux integral on the right-hand side vanishes, since the probability current at the boundary of the system must be 0. This property is important for the self-consistency of quantum mechanics: after we choose the normalization condition (2.2) at one time, the Schrödinger equation fixes the normalization for all other times.

2.6 The time independent Schrödinger equation

In the previous sections we have formulated the Schrödinger equation. In the case of a free particle, we have seen that a general wave function can be written as a superposition of plane waves. The peculiarity of plane waves is that they have a sharp energy value and thus their evolution in time is particularly simple. This then allows us to determine the propagation of a general wave function (we have explicitly calculated the example of a Gaussian wave packet).

With this motivation, let us now consider the wave functions of states with sharp energy E for a general Schrödinger equation (with potential). Because of the correspondence $E \rightarrow i\hbar\partial/\partial t$, these wave functions have the form

$$\psi(\mathbf{r}, t) = \Psi(\mathbf{r}) e^{-\frac{i}{\hbar} Et}, \quad (2.57)$$

with $\Psi(\mathbf{r})$ a function, which depends only on \mathbf{r} . Also in this case the time evolution is simple and the probability density $|\psi(\mathbf{r}, t)|^2 = |\Psi(\mathbf{r})|^2$ is time independent: therefore these wave functions are called *stationary*.

Inserting the wave function (2.57) in the Schrödinger equation (2.48) gives an equation for $\Psi(\mathbf{r})$:

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}). \quad (2.58)$$

We call this equation *time independent Schrödinger equation*. It represents an eigenvalue problem: $\Psi(\mathbf{r})$ is an eigenfunction of the Hamilton operator \hat{H} with energy eigenvalue E .

Let $\Psi_n(\mathbf{r})$ ($n \in \mathbb{N}$) be a complete set of normalized eigenfunctions of the Hamilton operator with energy eigenvalues E_n ,

$$\hat{H}\Psi_n(\mathbf{r}) = E_n\Psi_n(\mathbf{r}). \quad (2.59)$$

Then, analogously to the wave packet for free particles, one can write a general wave function as a superposition of stationary states. More precisely: suppose we know the wave function of a system $\psi(\mathbf{r}, 0)$ at time $t = 0$ and we want to determine the time evolution $\psi(\mathbf{r}, t)$, i.e. the solution of the Schrödinger equation (2.48). Then we can first write $\psi(\mathbf{r}, 0)$ as the superposition of the eigenfunctions,

$$\psi(\mathbf{r}, 0) = \sum_n a_n \Psi_n(\mathbf{r}), \quad (2.60)$$

with $a_n \in \mathbb{C}$. The time evolution is then simply

$$\psi(\mathbf{r}, t) = \sum_n a_n \Psi_n(\mathbf{r}) e^{-\frac{i}{\hbar} E_n t}. \quad (2.61)$$

It solves the Schrödinger equation (2.48), since every single term is a solution of the linear differential equation.

We have thus reduced the problem of finding the general solution $\psi(\mathbf{r}, t)$ of the Schrödinger equation (to a given initial condition $\psi(\mathbf{r}, 0)$), to finding the complete set of solutions of the time independent Schrödinger equation (2.59). Let us now apply this strategy on a simple example.

2.7 Energy eigenfunctions in an infinite potential well

We consider a one-dimensional system bounded by infinitely high walls, i.e., the potential (Fig. 2.2) is given by

$$V(x) = \begin{cases} 0, & -L/2 < x < L/2 \\ \infty, & \text{otherwise.} \end{cases} \quad (2.62)$$

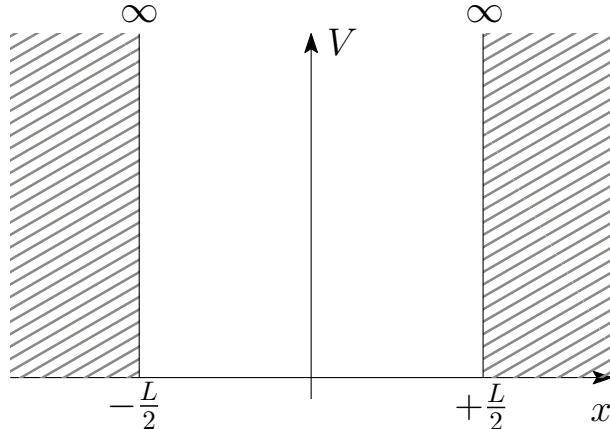


Figure 2.2: Potential of an infinite well.

We now want to determine the solutions of the time independent Schrödinger equation,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi(x) = E \Psi(x), \quad \text{for } |x| < \frac{L}{2}. \quad (2.63)$$

For $|x| \geq L/2$ the potential is infinite and it is impossible for a particle to be in this range. The interpretation of the wave function as the probability of finding the particle at a certain location requires that the wave function vanishes there. Furthermore, the wave function must be continuous⁵. Therefore it must go to zero at the walls, i.e., the boundary conditions are $\Psi(-L/2) = \Psi(+L/2) = 0$.

We solve equation (2.63) with the Ansatz

$$\Psi(x) = \begin{cases} A \cos(qx), & \text{even parity} \\ A \sin(qx), & \text{odd parity} \end{cases}. \quad (2.64)$$

Note that our system has a symmetry. It is invariant under reflection at $x = 0$, i.e. $x \rightarrow -x$. This symmetry operation, *parity*, now allows us to classify the states according to their even or odd parity, i.e. $\Psi(-x) = +\Psi(x)$ (even) or $\Psi(-x) = -\Psi(x)$ (odd). In this system, parity is a conserved quantity, i.e., a constant under time evolution. We will see in chapter 6 that there is a close relation between symmetries and conservation laws in quantum mechanics.

Inserting the Ansatz into the time independent Schrödinger equation yields the energy as a function of q ,

$$E = \frac{\hbar^2 q^2}{2m}. \quad (2.65)$$

The boundary conditions quantize q and thus also the energy eigenvalues: for the solutions of even parity we find

$$q_e = \frac{(2n-1)\pi}{L} \quad \Rightarrow \quad E_{e,n} = \frac{\hbar^2 \pi^2 (2n-1)^2}{2m L^2}, \quad (2.66)$$

⁵We will consider the boundary conditions in chapter 4, studying other one-dimensional potentials.

and for odd parity,

$$q_o = \frac{2\pi n}{L} \quad \Rightarrow \quad E_{o,n} = \frac{2\hbar^2\pi^2n^2}{mL^2}, \quad (2.67)$$

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

The system has a discrete energy spectrum. The state of lowest energy has not energy $E = 0$ as in classical physics, but $E_{g,1} = \hbar^2\pi^2/2mL^2$. This finite ground state energy is the result of the zero point motion, i.e., of the uncertainty principle. Obviously, if we make the potential narrower (L smaller), the ground state energy increases as the momentum increases.

The normalization of the wave function requires, for even parity, that

$$1 = |A|^2 \int_{-L/2}^{+L/2} dx \cos^2(qx) = |A|^2 \frac{L}{2}, \quad (2.68)$$

and analogously for odd parity, such that

$$A = \sqrt{\frac{2}{L}}. \quad (2.69)$$

The (time-independent) probability distribution for the particle in the energy eigenfunctions is thus

$$|\psi(x, t)|^2 = |\Psi(x)|^2 = \begin{cases} \frac{2}{L} \cos^2\left(\frac{\pi(2n-1)x}{L}\right), & \text{even parity} \\ \frac{2}{L} \sin^2\left(\frac{2\pi nx}{L}\right), & \text{odd parity} \end{cases} \quad (2.70)$$

and is shown in Fig. 2.3 for the 4 lowest energy eigenstates. We see an interference pattern like in a standing wave. With increasing quantum number the interference pattern becomes denser and denser. The “local mean” of the probability distribution is then the constant $\sim 1/L$ (averaged over a small spatial extent). This corresponds to the classical probability distribution that the particle can be found everywhere with the same probability.

For the expectation values we find, for example in the ground state:

$$\langle x \rangle = \frac{2}{L} \int_{-L/2}^{+L/2} dx x \cos^2\left(\frac{\pi}{L}x\right) = 0, \quad (2.71)$$

and

$$\langle p \rangle = \frac{2}{L} \int_{-L/2}^{+L/2} dx \cos\left(\frac{\pi}{L}x\right) \frac{\hbar}{i} \frac{\partial}{\partial x} \cos\left(\frac{\pi}{L}x\right) = 0, \quad (2.72)$$

in accordance with the symmetry of the system. These expectation values are time independent, since we calculated them for a pure energy eigenstate. For superpositions of energy eigenstates, the expectation values are generally time dependent.

Analogous calculations for the deviations give

$$\Delta x^2 = \langle x^2 \rangle = L^2 \left(\frac{1}{12} - \frac{1}{2\pi^2} \right), \quad (2.73)$$

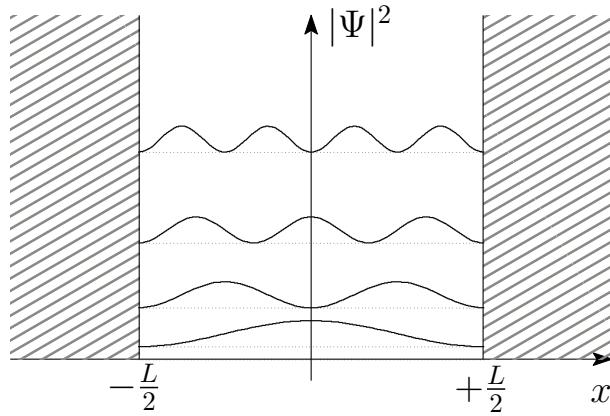


Figure 2.3: The probability density for the 4 lowest energy eigenstates in an infinite potential well.

and

$$\Delta p^2 = \langle p^2 \rangle = \frac{\hbar^2 \pi^2}{L^2}, \quad (2.74)$$

from which we find that

$$\Delta x \cdot \Delta p = \hbar \sqrt{\frac{\pi^2}{12} - \frac{1}{2}} \approx 0.568 \hbar > \frac{\hbar}{2}. \quad (2.75)$$

The solution clearly satisfies the Heisenberg's uncertainty principle, independently of the width L . At the same time we see that $p_0 = \sqrt{\langle p^2 \rangle} = \hbar\pi/L = q\hbar$. Therefore, it is clear that the ground state, interpreted as a standing wave, corresponds to the superposition of two counter-propagating waves with momentum $\pm p_0$. The same is also valid for the states with higher energy. The condition for an energy eigenstate is the realization of the standing wave (resonance) condition.

At the end of this section, we mention that if we use the potential in the form

$$V(x) = \begin{cases} 0, & 0 < x < L, \\ \infty, & \text{otherwise,} \end{cases} \quad (2.76)$$

then the energy eigenfunctions have the form

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad (2.77)$$

with energy eigenvalues

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}, \quad (2.78)$$

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

Chapter 3

General formulation of quantum mechanics

(1)

Schrödinger's wave mechanics is one of several formulations of quantum mechanics.

In addition, there is (historically shortly earlier) also Heisenberg's matrix mechanics.

At the end of the semester, we will discuss another version of quantum mechanics:

(3) the path integral formulation. Since all these formulations are equivalent, we want to introduce a common language, that it will allow to see the connections between these different approaches.

(2)

3.1 The Hilbert space

A quantum system corresponds to a set of quantum mechanical states. The Schrödinger wave functions $\psi(\mathbf{r}, t)$ are concrete representations of such states as functions in $L^2(V)$. We identify the quantum system with an abstract vector space \mathcal{H} , the Hilbert space, whose elements are the states of the system. More precisely, a Hilbert space is a vector space provided with a scalar product. In addition, the vector space must be complete with respect to the norm induced by the scalar product. We will discuss these aspects in more detail below.

Here, we first introduce the Dirac notation. A state (state vector) in \mathcal{H} is denoted by $|\alpha\rangle$, where α characterizes the state: depending on the case it can be a name, an index, a quantum number, We denote the corresponding dual state by $\langle\alpha|$. We call the state vectors $|\alpha\rangle$ "ket" and the dual state vectors $\langle\alpha|$ "bra", derived from the word "bracket":

$$\underbrace{\langle\alpha|}_{\text{bra}} \quad c \quad \underbrace{|\beta\rangle}_{\text{ket}}. \quad (3.1)$$

For example, if $\mathcal{H} = \mathbb{C}^n$ consists of column vectors with n components, then the

identification¹ holds:

$$\begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix} \rightarrow |\alpha\rangle. \quad (3.2)$$

Analogously, for the dual state vector we define

$$(a_1^*, a_2^*, \dots, a_n^*) \rightarrow \langle\alpha|. \quad (3.3)$$

From this, the scalar product in \mathbb{C}^n is obtained in a natural way: for two states $|\alpha\rangle$ and $|\beta\rangle$,

$$\begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix} \rightarrow |\alpha\rangle \quad \text{and} \quad \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix} \rightarrow |\beta\rangle, \quad (3.4)$$

the scalar product is given by

$$\langle\alpha|\beta\rangle = a_1^*b_1 + a_2^*b_2 + \dots + a_n^*b_n. \quad (3.5)$$

On the other hand, if $\mathcal{H} = L^2(V)$ consists of wave functions, then the identification holds:

$$\psi(\mathbf{r}) \rightarrow |\psi\rangle \quad \text{and} \quad \psi^*(\mathbf{r}) \rightarrow \langle\psi|. \quad (3.6)$$

The scalar product of two states $|\psi_1\rangle$ and $|\psi_2\rangle$ in $L^2(\mathbb{R}^3)$ is²:

$$\langle\psi_1|\psi_2\rangle = \int_V d^3r \psi_1^*(\mathbf{r})\psi_2(\mathbf{r}). \quad (3.7)$$

Let us now describe the abstract structure of a Hilbert space in more detail.

1. \mathcal{H} is a complex vector space

For all $|\alpha\rangle, |\beta\rangle \in \mathcal{H}$ holds,

$$|a\alpha + b\beta\rangle = a|\alpha\rangle + b|\beta\rangle \in \mathcal{H}, \quad \text{where } a, b \in \mathbb{C}. \quad (3.8)$$

Note the notation:

$$|a\alpha\rangle = a|\alpha\rangle \quad \text{and} \quad \langle a\alpha| = a^*\langle\alpha|. \quad (3.9)$$

The addition is commutative. There is a zero element $|0\rangle$, with $|\alpha\rangle + |0\rangle = |\alpha\rangle$. These properties are equivalent to the superposition principle.

¹We emphasize that this is an identification and not an equality: the left-hand side depends on the chosen basis, the right-hand side does not.

²Intuitively, this definition can be viewed as follows: a function ψ can be understood as a vector with infinitely many (and overcountable) components, namely the function values $\psi(\mathbf{r})$ for each vector $\mathbf{r} \in V \subset \mathbb{R}^3$. Then, for the scalar product, the discrete sum in (3.5) becomes the integral over the continuous variable \mathbf{r} . We will make this idea more precise in section 3.4.

The states $|\alpha_1\rangle, \dots, |\alpha_N\rangle$ are linear independent if

$$\sum_{n=1}^N a_n |\alpha_n\rangle = |0\rangle \quad (3.10)$$

is possible only for $a_1 = a_2 = \dots = a_N = 0$.

2. \mathcal{H} is unitary

There is a (complex) scalar product, i.e., for all pairs of states $|\alpha\rangle, |\beta\rangle \in \mathcal{H}$ we define a complex number $\langle\alpha|\beta\rangle$, with the properties:

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^*, \quad (3.11)$$

$$\langle\alpha|\beta + \gamma\rangle = \langle\alpha|\beta\rangle + \langle\alpha|\gamma\rangle, \quad (3.12)$$

$$\langle\alpha|c\beta\rangle = c\langle\alpha|\beta\rangle = \langle c^*\alpha|\beta\rangle, \quad (3.13)$$

$$\langle\alpha|\alpha\rangle > 0 \quad \text{if } |\alpha\rangle \neq |0\rangle \quad \text{and} \quad \langle 0|0\rangle = 0. \quad (3.14)$$

Two states $|\alpha\rangle$ and $|\beta\rangle$ are *orthogonal*, if

$$\langle\alpha|\beta\rangle = 0. \quad (3.15)$$

The *norm* of a state $|\alpha\rangle$ is defined by

$$\|\alpha\| = \sqrt{\langle\alpha|\alpha\rangle} \quad (3.16)$$

and a state is *normalized* if

$$\|\alpha\| = 1. \quad (3.17)$$

The triangle inequality applies here,

$$\|\alpha + \beta\| \leq \|\alpha\| + \|\beta\|, \quad (3.18)$$

together with the Cauchy-Schwarz inequality,

$$|\langle\alpha|\beta\rangle| \leq \|\alpha\|\|\beta\|. \quad (3.19)$$

3. \mathcal{H} is complete

Completeness of a vector space means that each Cauchy sequence $\{|\alpha_n\rangle\}$ converges in \mathcal{H} . I.e., if for each $\varepsilon > 0$ it exists a N such that $\|\alpha_n - \alpha_m\| < \varepsilon$ for all $m, n \geq N$, then there is a $|\alpha\rangle \in \mathcal{H}$ with $\lim_{n \rightarrow \infty} |\alpha_n\rangle = |\alpha\rangle$.

Until here the definition of Hilbert space: a unitary vector space which is complete with respect to the induced norm. We assume in addition that:

4. \mathcal{H} is separable

Separability means that there exists a countable set M of states $|\alpha_n\rangle \in \mathcal{H}$, such that each state $|\alpha\rangle \in \mathcal{H}$ can be arbitrarily good approximated with states from M , i.e., for each $\varepsilon > 0$ it exists a state $|\alpha_n\rangle \in M$ with $\|\alpha_n - \alpha\| < \varepsilon$.

Under these conditions, there exists a (countable) orthonormal basis of states $\{|\phi_n\rangle\}$,

$$\langle\phi_n|\phi_m\rangle = \delta_{nm}. \quad (3.20)$$

This basis allows to represent each state $|\alpha\rangle$ from \mathcal{H} with the projection on the basis states:

$$|\alpha\rangle = \sum_n \langle\phi_n|\alpha\rangle |\phi_n\rangle, \quad (3.21)$$

where the scalar product $\langle\phi_n|\alpha\rangle$ gives the component of $|\alpha\rangle$ in the direction of $|\phi_n\rangle$. In other words, the operator

$$\hat{P}_n = |\phi_n\rangle\langle\phi_n| \quad (3.22)$$

is the projection on the state $|\phi_n\rangle$:

$$\hat{P}_n|\alpha\rangle = |\phi_n\rangle\langle\phi_n|\alpha\rangle, \quad (3.23)$$

with $\hat{P}_n^2 = \hat{P}_n$ (since $\langle\phi_n|\phi_n\rangle = 1$). From this, we get the *completeness relation*,

$$\sum_n |\phi_n\rangle\langle\phi_n| = 1, \quad (3.24)$$

i.e., a *representation of the identity operator* as sum over the whole orthonormal basis. The Parseval identity for the state $|\alpha\rangle$ represented in equation (3.21) also holds:

$$\|\alpha\|^2 = \sum_n |\langle\phi_n|\alpha\rangle|^2. \quad (3.25)$$

We will now consider an example: the infinite potential well from section (2.7), with width $L = 2$. The stationary states are given by the wave functions (in the representation of equation (2.77)):

$$\Psi_n(x) = \sin\left(\frac{n\pi x}{2}\right) \rightarrow |\Psi_n\rangle. \quad (3.26)$$

The set $\{|\Psi_n\rangle\}$ is an orthonormal system in the vector space \mathcal{H} of all states which have a finite wave function in the interval $0 < x < 2$, and which vanish at $x = 0$ and $x = 2$. The orthonormality follows from

$$\langle\Psi_n|\Psi_m\rangle = \int_0^2 dx \sin\left(\frac{n\pi x}{2}\right) \sin\left(\frac{m\pi x}{2}\right) = \delta_{nm}. \quad (3.27)$$

Any wave function $\Phi(x)$ in \mathcal{H} can be periodically extended as an odd function (because $\Phi(0) = \Phi(2) = 0$), with period $2L = 4$. Such a function can be represented as a Fourier series and, because it is odd, only sine functions occur in the series. These sine functions are exactly the wave functions (3.26) of the stationary states. It follows that each wave function $\Phi(x)$ in \mathcal{H} can be written as a superposition of the stationary states,

$$|\Phi\rangle = \sum_n b_n |\Psi_n\rangle, \quad (3.28)$$

with the coefficients

$$b_n = \langle \Psi_n | \Phi \rangle = \int_0^2 dx \sin\left(\frac{n\pi x}{2}\right) \Phi(x), \quad (3.29)$$

where $|b_n|^2$ is the probability to measure the energy eigenvalue E_n during an energy measurement at the state $|\Phi\rangle$. It follows that the system $\{|\Psi_n\rangle\}$ is an orthonormal basis of \mathcal{H} . Therefore \mathcal{H} is complete and separable (the basis is countable).

3.2 Linear operators

We consider now linear operators acting on the Hilbert space \mathcal{H} . An operator \hat{A} assigns a new state in \mathcal{H} to a state in \mathcal{H} :

$$|\beta\rangle = \hat{A}|\alpha\rangle, \quad (3.30)$$

where $|\alpha\rangle$ is in the domain of \hat{A} , i.e., $|\alpha\rangle \in D_{\hat{A}} \subset \mathcal{H}$, and $|\beta\rangle$ is in the range of \hat{A} , i.e., $|\beta\rangle \in R_{\hat{A}} \subset \mathcal{H}$. For “bra” vectors it holds then:

$$\langle \beta | = \langle \alpha | \hat{A}^\dagger. \quad (3.31)$$

The operator \hat{A} is linear, if

$$\hat{A}(a_1|\alpha_1\rangle + a_2|\alpha_2\rangle) = a_1\hat{A}|\alpha_1\rangle + a_2\hat{A}|\alpha_2\rangle, \quad (3.32)$$

for all $|\alpha_1\rangle, |\alpha_2\rangle \in D_{\hat{A}}$.

We introduce the operator adjoint to \hat{A} as the operator \hat{A}^\dagger , with

$$\langle \beta | \hat{A} | \alpha \rangle = \langle \alpha | \hat{A}^\dagger | \beta \rangle^*, \quad (3.33)$$

which uniquely defines the adjoint operator. For products of operators it holds

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger. \quad (3.34)$$

We call an operator \hat{A} Hermitian (or self-adjoint), if

$$\hat{A} = \hat{A}^\dagger. \quad (3.35)$$

With the help of the completeness relation (3.24), operators in the Dirac notation can be represented in any orthonormal basis as matrices. In the basis $\{|n\rangle\}$ it holds

$$\hat{A} = \left(\sum_m |m\rangle \langle m| \right) \hat{A} \left(\sum_n |n\rangle \langle n| \right) = \sum_{m,n} A_{mn} |m\rangle \langle n|, \quad (3.36)$$

where $A_{mn} = \langle m | \hat{A} | n \rangle$ corresponds to a matrix element. The adjoint operator is then

$$\hat{A}^\dagger = \sum_{m,n} A_{nm}^* |m\rangle \langle n|. \quad (3.37)$$

It follows that for a Hermitian operator, the matrix (with respect to an orthonormal basis) is a Hermitian matrix, i.e., by transposing and complex conjugating the matrix, one gets the same matrix: $A_{nm}^* = A_{mn}$.

The commutator of two operators is

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad (3.38)$$

and satisfies the relations

$$[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}, \quad (3.39)$$

and

$$[\hat{A}, \hat{B}]^\dagger = [\hat{B}^\dagger, \hat{A}^\dagger]. \quad (3.40)$$

A function of an operator is defined by the Taylor expansion,

$$f(\hat{A}) = \sum_n \frac{1}{n!} f^{(n)}(0) \hat{A}^n. \quad (3.41)$$

For the exponential function one finds then

$$e^{\hat{A}} = \sum_{n=0}^{\infty} \frac{\hat{A}^n}{n!}. \quad (3.42)$$

Furthermore,

$$e^{\hat{A}} e^{\hat{B}} = e^{\hat{A} + \hat{B} + \frac{1}{2}[\hat{A}, \hat{B}] + \frac{1}{12}[\hat{A}, [\hat{A}, \hat{B}]] - \frac{1}{12}[\hat{B}, [\hat{A}, \hat{B}]] + \dots} \quad (3.43)$$

is the Baker-Campbell-Hausdorff formula. If $[\hat{A}, \hat{B}] = 0$, then

$$e^{\hat{A}} e^{\hat{B}} = e^{\hat{A} + \hat{B}} = e^{\hat{B}} e^{\hat{A}}. \quad (3.44)$$

If $[\hat{A}, \hat{B}] \neq 0$ but commutes with \hat{A} and \hat{B} , then:

$$e^{\hat{A}} e^{\hat{B}} = e^{\hat{B}} e^{\hat{A}} e^{[\hat{A}, \hat{B}]}, \quad (3.45)$$

$$e^{\hat{A} + \hat{B}} = e^{\hat{A}} e^{\hat{B}} e^{-\frac{1}{2}[\hat{A}, \hat{B}]}.$$

Furthermore, one can show:

$$e^{\hat{A}} \hat{B} e^{-\hat{A}} = \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!} [\hat{A}, [\hat{A}, \hat{B}]] + \dots \quad (3.47)$$

An operator \hat{U} is unitary, if

$$\hat{U}^\dagger \hat{U} = \hat{1}, \quad (3.48)$$

i.e., if $\hat{U}^{-1} = \hat{U}^\dagger$. Unitary operators leave the scalar product and the norm of states unchanged: for \hat{U} unitary is the scalar product of $\hat{U}|\alpha\rangle$ with $\hat{U}|\beta\rangle$,

$$\langle \alpha | \hat{U}^\dagger \hat{U} | \beta \rangle = \langle \alpha | \beta \rangle, \quad (3.49)$$

equal to the scalar probability of $|\alpha\rangle$ with $|\beta\rangle$. Analogously, the squared norm of $\hat{U}|\alpha\rangle$,

$$\langle \alpha | \hat{U}^\dagger \hat{U} | \alpha \rangle = \langle \alpha | \alpha \rangle, \quad (3.50)$$

is equal to the squared norm of $|\alpha\rangle$. For \hat{A} Hermitian and $\kappa \in \mathbb{R}$, the operator $e^{i\kappa A}$ is unitary:

$$(e^{i\kappa A})^\dagger = e^{-i\kappa A^\dagger} = e^{-i\kappa A} \Rightarrow (e^{i\kappa A})^\dagger (e^{i\kappa A}) = \hat{1}. \quad (3.51)$$

3.3 Hermitian operators

Hermitian operators (with $\hat{A}^\dagger = \hat{A}$) have a special place in quantum mechanics, because physical observables are described by such operators. The reason is that the expectation value $\langle A \rangle$ in the state $|\psi\rangle$ of an operator \hat{A} is given by

$$\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle, \quad (3.52)$$

as we have seen at the examples of position and momentum expectation values in chapter 2. But these expectation values must be real in order to express physical quantities, i.e.

$$\langle \psi | \hat{A} | \psi \rangle = \langle \psi | \hat{A} | \psi \rangle^* \quad (3.53)$$

for all states $|\psi\rangle$. But, with the definition of the adjoint operator (3.33),

$$\langle \psi | \hat{A} | \psi \rangle^* = \langle \psi | \hat{A}^\dagger | \psi \rangle. \quad (3.54)$$

It follows

$$\langle \psi | \hat{A} | \psi \rangle = \langle \psi | \hat{A}^\dagger | \psi \rangle, \quad (3.55)$$

for all states $|\psi\rangle$. Therefore $\hat{A}^\dagger = \hat{A}$ must hold: the operator is Hermitian.

We now want to understand the eigenvalues and eigenstates of a Hermitian operator. Let $|\alpha_n\rangle$ be a normalized eigenstate of a Hermitian operator \hat{A} with eigenvalue a_n ,

$$\hat{A}|\alpha_n\rangle = a_n|\alpha_n\rangle. \quad (3.56)$$

The eigenvalue is then real, since

$$\langle \alpha_n | \hat{A} | \alpha_n \rangle = \underbrace{\langle \alpha_n |}_{\text{real}} \underbrace{a_n}_{\text{real}} \underbrace{|\alpha_n \rangle}_{\text{real}} = a_n \langle \alpha_n | \alpha_n \rangle = a_n, \quad (3.57)$$

i.e., the eigenvalue a_n is the expectation value of \hat{A} in the state $|\alpha_n\rangle$ and as remarked above, the expectation values of Hermitian operators are all real.

The eigenstates $|\alpha_n\rangle$ and $|\alpha_m\rangle$ belonging to different eigenvalues a_n and $a_m \in \mathbb{R}$ are orthogonal, since from $\hat{A} = \hat{A}^\dagger$ one gets:

$$\begin{aligned} 0 &= \langle \alpha_m | \hat{A} | \alpha_n \rangle - \langle \alpha_m | \hat{A}^\dagger | \alpha_n \rangle \\ &= \langle \alpha_m | \hat{A} | \alpha_n \rangle - \langle \alpha_n | \hat{A} | \alpha_m \rangle^* \\ &= a_n \langle \alpha_m | \alpha_n \rangle - a_m^* \langle \alpha_n | \alpha_m \rangle^* \\ &= (a_n - a_m) \langle \alpha_m | \alpha_n \rangle. \end{aligned} \quad (3.58)$$

But $a_n \neq a_m$ and therefore $\langle \alpha_m | \alpha_n \rangle = 0$ must hold. In addition, the eigenstates belonging to the same eigenvalue can be chosen to be orthogonal and thus the eigenstates of a Hermitian operator form an orthonormal system, $\langle \alpha_m | \alpha_n \rangle = \delta_{mn}$. One can even show that the system is complete, as in the case of the energy eigenstates of the infinite potential well: the eigenstates of a Hermitian operator form an orthonormal basis.

If two Hermitian operators \hat{A} and \hat{B} commutes, i.e., $[\hat{A}, \hat{B}] = 0$, then they have common eigenstates $|\alpha_n\rangle$, which form an orthonormal basis, and vice versa:

$$\hat{A}|\alpha_n\rangle = a_n|\alpha_n\rangle \quad \text{and} \quad \hat{B}|\alpha_n\rangle = b_n|\alpha_n\rangle \quad \Leftrightarrow \quad \hat{B}\hat{A}|\alpha_n\rangle = \hat{A}\hat{B}|\alpha_n\rangle = a_n b_n |\alpha_n\rangle. \quad (3.59)$$

The knowledge of the eigenvalues a_n and of the eigenstates $|\alpha_n\rangle$ allows the *spectral representation* of a Hermitian operator,

$$\hat{A} = \sum_n a_n |\alpha_n\rangle \langle \alpha_n|, \quad (3.60)$$

because of the matrix representation (3.36), with the observation that in this case the matrix is diagonal:

$$A_{mn} = \langle \alpha_m | \hat{A} | \alpha_n \rangle = a_n \langle \alpha_m | \alpha_n \rangle = a_n \delta_{mn}. \quad (3.61)$$

We consider now an arbitrary state $|\psi\rangle$. We can write $|\psi\rangle$ using the basis consisting of the eigenstates $|\alpha_n\rangle$ of the operator \hat{A} :

$$|\psi\rangle = \sum_n \langle \alpha_n | \psi \rangle |\alpha_n\rangle. \quad (3.62)$$

It follows that the expectation value of the operator \hat{A} in this state is

$$\begin{aligned} \langle \hat{A} \rangle &= \langle \psi | \hat{A} | \psi \rangle \\ &= \left(\sum_m \langle \alpha_m | \psi \rangle^* \langle \alpha_m | \right) \hat{A} \left(\sum_n |\alpha_n\rangle \langle \alpha_n | \psi \rangle \right) \\ &= \sum_{m,n} \langle \alpha_m | \hat{A} | \alpha_n \rangle |\langle \alpha_n | \psi \rangle|^2 \\ &= \sum_n a_n |\langle \alpha_n | \psi \rangle|^2. \end{aligned} \quad (3.63)$$

Here $|\langle \alpha_n | \psi \rangle|^2$ corresponds to the probability to find the state $|\alpha_n\rangle$ in the state $|\psi\rangle$. The expectation value in the state $|\psi\rangle$ is the average of the eigenvalues a_n weighted with these probabilities. In other words, if the physical quantity A belonging to the operator \hat{A} is measured in the state $|\psi\rangle$, then the possible measured values are the eigenvalues of the operator: the eigenvalue a_n is measured with probability $|\langle \alpha_n | \psi \rangle|^2$.

As we saw in section 2.6, the eigenstates of the Hamilton operator \hat{H} form a particularly important orthonormal basis, because they correspond to the stationary states. Let $|\Psi_n\rangle$ be an eigenstate of \hat{H} with energy eigenvalue E_n ,

$$\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle, \quad (3.64)$$

then the spectral representation of \hat{H} is

$$\hat{H} = \sum_n E_n |\Psi_n\rangle \langle \Psi_n|. \quad (3.65)$$

If we know the state $|\Phi(0)\rangle$ of the system at time $t = 0$ as a linear combination of the energy eigenstates,

$$|\Phi(0)\rangle = \sum_n \langle \Psi_n | \Phi(0) \rangle |\Psi_n\rangle, \quad (3.66)$$

then the state at a later time t is given by

$$|\Phi(t)\rangle = \sum_n \langle \Psi_n | \Phi(0) \rangle e^{-\frac{i}{\hbar} E_n t} |\Psi_n\rangle. \quad (3.67)$$

3.4 Position space and momentum space representations

It is possible to describe the position space representation and the momentum space representation of chapter 2 using Dirac notation. For this purpose we consider the two special bases,

$$|r\rangle \rightarrow \text{particle at position } r, \quad (3.68)$$

$$|p\rangle \rightarrow \text{particle with momentum } p, \quad (3.69)$$

each of which is a complete basic set: $\{|r\rangle | r \in \mathbb{R}^3\}$ and $\{|p\rangle | p \in \mathbb{R}^3\}$. They are also orthonormal, in the following sense:

$$\langle r | r' \rangle = \delta^{(3)}(r - r') \quad (3.70)$$

and

$$\langle p | p' \rangle = (2\pi\hbar)^3 \delta^{(3)}(p - p'). \quad (3.71)$$

The state $|r'\rangle$ is localized at the place r' : its projection on $|r\rangle$ is equal to 0 if $r \neq r'$. If $r = r'$, the scalar product gives a δ distribution instead of a Kronecker δ , because the position is continuously distributed (not discrete as in (3.20)).

For the same reason, the identity operator corresponds to

$$1 = \int d^3r |r\rangle \langle r| = \int \frac{d^3p}{(2\pi\hbar)^3} |p\rangle \langle p|, \quad (3.72)$$

with an integration over the continuous variable instead of the discrete sum. If we consider a general state $|\psi\rangle$, then $\langle r | \psi \rangle$ is its component at location r , i.e., the probability amplitude of finding the particle in r . It follows:

$$\langle r | \psi \rangle = \psi(r), \quad \text{position space wave function of the particle}, \quad (3.73)$$

$$\langle p | \psi \rangle = \tilde{\psi}(p), \quad \text{momentum space wave function of the particle}. \quad (3.74)$$

This means that, analogously to the sum (3.21),

$$|\psi\rangle = \int d^3r \psi(r) |r\rangle = \int \frac{d^3p}{(2\pi\hbar)^3} \tilde{\psi}(p) |p\rangle \quad (3.75)$$

and

$$\langle \psi | = \int d^3r \psi(\mathbf{r})^* \langle \mathbf{r} | = \int \frac{d^3p}{(2\pi\hbar)^3} \tilde{\psi}(\mathbf{p})^* \langle \mathbf{p} |. \quad (3.76)$$

The scalar product of two states $|\psi\rangle$ and $|\psi'\rangle$ is then

$$\begin{aligned} \langle \psi | \psi' \rangle &= \int d^3r \int d^3r' \psi(\mathbf{r})^* \psi'(\mathbf{r}') \underbrace{\langle \mathbf{r} | \mathbf{r}' \rangle}_{\delta^{(3)}(\mathbf{r} - \mathbf{r}')} \\ &= \int d^3r \psi(\mathbf{r})^* \psi'(\mathbf{r}), \end{aligned} \quad (3.77)$$

i.e., just the scalar product for wave functions in $L^2(\mathbb{R}^3)$.

We have seen that the basis change corresponds to a Fourier transformation,

$$\tilde{\psi}(\mathbf{p}) = \int d^3r e^{-\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}} \psi(\mathbf{r}). \quad (3.78)$$

In this formalism,

$$|\mathbf{p}\rangle = \int d^3r |\mathbf{r}\rangle \langle \mathbf{r} | \mathbf{p}\rangle, \quad (3.79)$$

where $\langle \mathbf{r} | \mathbf{p}\rangle$ represents the transformation matrix. From

$$\tilde{\psi}(\mathbf{p}) = \langle \mathbf{p} | \psi \rangle = \int d^3r \langle \mathbf{p} | \mathbf{r} \rangle \underbrace{\langle \mathbf{r} | \psi \rangle}_{\psi(\mathbf{r})}, \quad (3.80)$$

and (3.78) follows:

$$\langle \mathbf{p} | \mathbf{r} \rangle = e^{-\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}}, \quad \langle \mathbf{r} | \mathbf{p} \rangle = \langle \mathbf{p} | \mathbf{r} \rangle^* = e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}}. \quad (3.81)$$

Spectral Representation

The states $|\mathbf{r}\rangle$ are eigenstates of the position operator $\hat{\mathbf{r}}$ with eigenvalue \mathbf{r} ,

$$\hat{\mathbf{r}} |\mathbf{r}\rangle = \mathbf{r} |\mathbf{r}\rangle, \quad (3.82)$$

and the position operator can thereby be written in the spectral representation

$$\hat{\mathbf{r}} = \int d^3r \mathbf{r} |\mathbf{r}\rangle \langle \mathbf{r}|. \quad (3.83)$$

Analogously the states $|\mathbf{p}\rangle$ are eigenstates of the momentum operator $\hat{\mathbf{p}}$ with eigenvalue \mathbf{p} ,

$$\hat{\mathbf{p}} |\mathbf{p}\rangle = \mathbf{p} |\mathbf{p}\rangle, \quad (3.84)$$

and the spectral representation of the momentum operator is

$$\hat{\mathbf{p}} = \int \frac{d^3p}{(2\pi\hbar)^3} \mathbf{p} |\mathbf{p}\rangle \langle \mathbf{p}|. \quad (3.85)$$

Using the representation of the identity operator (3.72), the expectation value of the position operator for the state $|\psi\rangle$ is then

$$\langle \psi | \hat{\mathbf{r}} | \psi \rangle = \int d^3r d^3r' \underbrace{\langle \psi | \mathbf{r} \rangle}_{\psi^*(\mathbf{r})} \underbrace{\langle \mathbf{r} | \hat{\mathbf{r}} | \mathbf{r}' \rangle}_{\mathbf{r} \delta^{(3)}(\mathbf{r} - \mathbf{r}')} \underbrace{\langle \mathbf{r}' | \psi \rangle}_{\psi(\mathbf{r}')} = \int d^3r \mathbf{r} |\psi(\mathbf{r})|^2, \quad (3.86)$$

as in (2.13). The expectation value of the momentum operator is

$$\langle \psi | \hat{\mathbf{p}} | \psi \rangle = \int d^3 r d^3 r' \langle \psi | \mathbf{r} \rangle \langle \mathbf{r} | \hat{\mathbf{p}} | \mathbf{r}' \rangle \langle \mathbf{r}' | \psi \rangle \stackrel{!}{=} \int d^3 r \psi^*(\mathbf{r}) \frac{\hbar}{i} \nabla \psi(\mathbf{r}), \quad (3.87)$$

from which we get:

$$\langle \mathbf{r} | \hat{\mathbf{p}} | \mathbf{r}' \rangle = \delta^{(3)}(\mathbf{r} - \mathbf{r}') \frac{\hbar}{i} \nabla. \quad (3.88)$$

If we use the momentum space representation, then this expectation value is

$$\langle \psi | \hat{\mathbf{p}} | \psi \rangle = \int \frac{d^3 p}{(2\pi\hbar)^3} \mathbf{p} |\tilde{\psi}(\mathbf{p})|^2, \quad (3.89)$$

and

$$\langle \mathbf{p} | \hat{\mathbf{p}} | \mathbf{p}' \rangle = (2\pi\hbar)^3 \mathbf{p} \delta^{(3)}(\mathbf{p} - \mathbf{p}'). \quad (3.90)$$

3.5 Postulates of quantum mechanics

Using this language, the postulates of quantum mechanics can be reformulated.

P1: Each state of a quantum mechanical system is described by an element $|\psi\rangle$ in the Hilbert space \mathcal{H} .

P2: The measurable quantities (observables) correspond to Hermitian operators, e.g. the position operator $\hat{\mathbf{r}}$.

P3: The expectation value (average) $\langle \hat{A} \rangle$ of an observable A in a given state $|\psi\rangle$ is given by the scalar product $\langle \psi | \psi' \rangle$, where $|\psi'\rangle = \hat{A}|\psi\rangle$, i.e.,

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle. \quad (3.91)$$

P4: The time evolution of the states is determined by the Hamilton operator \hat{H} (equivalent to the Schrödinger equation),

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle. \quad (3.92)$$

For a time independent Hamilton operator \hat{H} , it follows that

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar} \hat{H} t} |\psi(0)\rangle \quad (3.93)$$

is the solution of the Schrödinger equation.

In the simplest case of a single-particle system, the Hamilton operator has the form

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}}) \quad (3.94)$$

and corresponds to the classical Hamilton function, where the position and momentum coordinates are replaced by their corresponding Hermitian operators. If we multiply the operator from the left with $\langle \mathbf{r} |$ and from the right with $|\psi(t)\rangle$, we obtain the Schrödinger equation in the position space representation (2.44). Equivalent Schrödinger equations can therefore be defined in any orthonormal basis.

P5: If during a measurement of the observable A the eigenvalue a_n was measured, then the state of the system changes to the corresponding eigenstate $|\alpha_n\rangle$. For an operator \hat{A} only the eigenvalues can occur as a result of the measurement. The probability, to get the measurement result a_n for the state $|\psi\rangle$ is given by $|\langle\alpha_n|\psi\rangle|^2$. Thus the expectation value of \hat{A} is

$$\langle\hat{A}\rangle = \langle\psi|\hat{A}|\psi\rangle = \sum_n \langle\psi|\hat{A}|\alpha_n\rangle\langle\alpha_n|\psi\rangle = \sum_n a_n |\langle\alpha_n|\psi\rangle|^2. \quad (3.95)$$

3.6 Heisenberg's uncertainty relation

We now want to derive the generalized uncertainty relation from the postulates. We consider two Hermitian operators \hat{A} and \hat{B} , which correspond to observables. For any state $|\psi\rangle$ the squared standard deviation from the expectation value is defined as

$$\Delta A^2 = \langle\psi|(\hat{A} - \langle\hat{A}\rangle)^2|\psi\rangle \quad \text{and} \quad \Delta B^2 = \langle\psi|(\hat{B} - \langle\hat{B}\rangle)^2|\psi\rangle. \quad (3.96)$$

We define the states $|a\rangle$ and $|b\rangle$ by

$$|a\rangle = (\hat{A} - \langle\hat{A}\rangle)|\psi\rangle \quad \text{and} \quad |b\rangle = (\hat{B} - \langle\hat{B}\rangle)|\psi\rangle, \quad (3.97)$$

such that

$$\langle a| = \langle\psi|(\hat{A} - \langle\hat{A}\rangle)^\dagger \quad \text{and} \quad \langle b| = \langle\psi|(\hat{B} - \langle\hat{B}\rangle)^\dagger. \quad (3.98)$$

It follows (since $\hat{A}^\dagger = \hat{A}$)

$$\begin{aligned} \langle a|a\rangle &= \langle\psi|(\hat{A} - \langle\hat{A}\rangle)^\dagger(\hat{A} - \langle\hat{A}\rangle)|\psi\rangle \\ &= \langle\psi|(\hat{A} - \langle\hat{A}\rangle)^2|\psi\rangle \\ &= \Delta A^2, \end{aligned} \quad (3.99)$$

i.e., just the squared standard deviation for the operator \hat{A} . Analogously for \hat{B} : $\Delta B^2 = \langle b|b\rangle$. The Cauchy-Schwarz inequality gives $|\langle a|b\rangle|^2 \leq \langle a|a\rangle\langle b|b\rangle$ and therefore

$$(\Delta A)^2(\Delta B)^2 \geq |\langle a|b\rangle|^2 \geq |\text{Im}\langle a|b\rangle|^2 = \left| \frac{\langle a|b\rangle - \langle b|a\rangle}{2i} \right|^2. \quad (3.100)$$

We can calculate $\langle a|b\rangle$:

$$\begin{aligned} \langle a|b\rangle &= \langle\psi|(\hat{A} - \langle\hat{A}\rangle)(\hat{B} - \langle\hat{B}\rangle)|\psi\rangle \\ &= \langle\psi|\hat{A}\hat{B} - \langle\hat{A}\rangle\hat{B} - \hat{A}\langle\hat{B}\rangle + \langle\hat{A}\rangle\langle\hat{B}\rangle|\psi\rangle \\ &= \langle\hat{A}\hat{B}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle. \end{aligned} \quad (3.101)$$

And analogously $\langle b|a\rangle = \langle\hat{B}\hat{A}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle$. This results in the generalized uncertainty relation,

$$\Delta A \cdot \Delta B \geq \frac{1}{2}|\langle\psi|[\hat{A}, \hat{B}]|\psi\rangle|. \quad (3.102)$$

We note that the commutator $[\hat{A}, \hat{B}]$ decides whether and to what extent the two observables can be determined simultaneously: if \hat{A} and \hat{B} commute, $[\hat{A}, \hat{B}] = 0$,

then both observables can be known exactly. This is consistent with the fact that commutative operators have common eigenstates that form an orthonormal basis. If, on the other hand, \hat{A} and \hat{B} do not commute, then one cannot simultaneously determine the observables with arbitrary precision (and the basis of common eigenstates does not exist).

As an example we consider position and momentum operator ($\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}_x$): we need therefore the commutator $[\hat{x}, \hat{p}_x]$. We can for example calculate it in the position space representation:

$$\begin{aligned} [\hat{x}, \hat{p}_x]\phi(x) &= \left(x \frac{\hbar}{i} \frac{\partial}{\partial x} - \frac{\hbar}{i} \frac{\partial}{\partial x} x \right) \phi(x) \\ &= \frac{\hbar}{i} x \phi'(x) - \frac{\hbar}{i} (x \phi(x))' \\ &= -\frac{\hbar}{i} \phi(x), \end{aligned} \quad (3.103)$$

for all wave functions $\phi(x)$. Therefore,

$$[\hat{x}, \hat{p}_x] = i\hbar. \quad (3.104)$$

Inserting in (3.102) gives the known Heisenberg's uncertainty relation

$$\Delta x \cdot \Delta p_x \geq \frac{1}{2} |\langle \psi | i\hbar | \psi \rangle| = \frac{\hbar}{2}. \quad (3.105)$$

If, on the other hand, one considers a coordinate and a momentum in a different direction, e.g. y and p_x , then one finds $[\hat{y}, \hat{p}_x] = 0$, i.e. one can exactly determine y and p_x at the same time and $\Delta y \cdot \Delta p_x \geq 0$.

3.7 Heisenberg's matrix mechanics

So far we have considered the *Schrödinger representation* of quantum mechanics, in which the states describe the time evolution of the system. If the Hamilton operator \hat{H} is time independent, then the time evolution of a state is described by the unitary operator $e^{-i\hat{H}t/\hbar}$:

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}\hat{H}t}|\psi(0)\rangle. \quad (3.106)$$

The expectation value of an operator as function of time is given by

$$\langle \hat{A} \rangle(t) = \langle \psi(t) | \hat{A} | \psi(t) \rangle. \quad (3.107)$$

Instead of using the time-dependent states, however, we can also map the time dependency to the operator, i.e.:

$$\langle \hat{A} \rangle(t) = \langle \psi(0) | e^{\frac{i}{\hbar}\hat{H}t} \hat{A} e^{-\frac{i}{\hbar}\hat{H}t} | \psi(0) \rangle = \langle \psi(0) | \hat{A}(t) | \psi(0) \rangle, \quad (3.108)$$

with

$$\hat{A}(t) = e^{\frac{i}{\hbar}\hat{H}t} \hat{A} e^{-\frac{i}{\hbar}\hat{H}t}. \quad (3.109)$$

This formulation is called *Heisenberg representation*. In this representation, the states are constant (equal to the “initial condition” $|\psi(0)\rangle$) and all the time dependence is in the operators. Of course, the result for the expectation values must be the same in the two representations.

The time-dependent operator $\hat{A}(t)$ must satisfy the equation of motion:

$$\frac{d}{dt}\hat{A}(t) = \frac{i}{\hbar}[\hat{H}, \hat{A}(t)], \quad (3.110)$$

as one can easily verify. Furthermore, the equations of motion for the operators also describe the evolution of the expectation values:

$$\frac{d}{dt}\langle\hat{A}\rangle(t) = \frac{i}{\hbar}\langle[\hat{H}, \hat{A}(t)]\rangle. \quad (3.111)$$

Consider, for example, a particle whose dynamics is described by $\hat{H} = \hat{\mathbf{p}}^2/2m + V(\hat{\mathbf{r}})$. We want to determine the equations of motion for the expectation values of the position and momentum operators. For this we need e.g.

$$\begin{aligned} [\hat{H}, \hat{x}(t)] &= [\hat{H}, e^{\frac{i}{\hbar}\hat{H}t}\hat{x}e^{-\frac{i}{\hbar}\hat{H}t}] \\ &= e^{\frac{i}{\hbar}\hat{H}t} \left[\frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{\mathbf{r}}), \hat{x} \right] e^{-\frac{i}{\hbar}\hat{H}t} \\ &= e^{\frac{i}{\hbar}\hat{H}t} \left(\frac{\hat{p}_x}{2m} [\hat{p}_x, \hat{x}] + [\hat{p}_x, \hat{x}] \frac{\hat{p}_x}{2m} \right) e^{-\frac{i}{\hbar}\hat{H}t} \\ &= -\frac{i\hbar}{m} e^{\frac{i}{\hbar}\hat{H}t} \hat{p}_x e^{-\frac{i}{\hbar}\hat{H}t} \\ &= -\frac{i\hbar}{m} \hat{p}_x(t) \end{aligned} \quad (3.112)$$

where we used (3.39) and furthermore that $[\hat{p}_x, \hat{x}] = -i\hbar$, $[\hat{p}_y, \hat{x}] = 0$ and $[\hat{p}_z, \hat{x}] = 0$ hold. It follows that

$$[\hat{H}, \hat{\mathbf{r}}(t)] = -\frac{i\hbar}{m} \hat{\mathbf{p}}(t). \quad (3.113)$$

Analogously, one can show:

$$[\hat{H}, \hat{\mathbf{p}}(t)] = i\hbar \nabla V(\hat{\mathbf{r}}(t)). \quad (3.114)$$

Thus, the so-called *Ehrenfest theorem* for the expectation values of the position and momentum operators results from the above equations,

$$\frac{d}{dt}\langle\hat{\mathbf{r}}\rangle = \frac{\langle\hat{\mathbf{p}}\rangle}{m} \quad (3.115)$$

$$\frac{d}{dt}\langle\hat{\mathbf{p}}\rangle = -\langle\nabla V(\hat{\mathbf{r}})\rangle, \quad (3.116)$$

from which we get, by combining the two equations,

$$m \frac{d^2}{dt^2}\langle\hat{\mathbf{r}}\rangle = -\langle\nabla V(\hat{\mathbf{r}})\rangle = \langle\mathbf{F}(\hat{\mathbf{r}})\rangle, \quad (3.117)$$

with $\mathbf{F} = -\nabla V$ as force. This is of course very similar to Newton's equation of motion in classical mechanics. However, one finds in general

$$\langle \mathbf{F}(\hat{\mathbf{r}}) \rangle \neq \mathbf{F}(\langle \hat{\mathbf{r}} \rangle), \quad (3.118)$$

so that the equivalence does not hold strictly.

Chapter 4

Quantum mechanics in one spatial dimension

In this chapter we come back to the concrete representation of quantum systems in the Schrödinger formulation. The aim is here, on the basis of a representative spectrum of simple systems in one spatial dimension, to introduce some of the most important concepts of quantum mechanics. These include, among others, the discrete energy spectra of bound states and the continuous spectra of extended states, the scattering of particles and their “tunneling” through potential barriers, as well as the energy bands of periodic potentials.

4.1 The harmonic oscillator

The **harmonic oscillator** is one of the few problems in quantum mechanics, which can be solved exactly in all dimensions. In this role, the harmonic oscillator is the basis for further developments of quantum mechanics, such as quantum field theory. The classical potential of a **harmonic oscillator** with frequency ω and mass m is $V(x) = m\omega^2 x^2/2$. The Hamilton operator is thus:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2. \quad (4.1)$$

We are interested in the stationary states, i.e., in the eigenstates of the Hamilton operator \hat{H} . This leads to the following **Schrödinger equation** in the position representation:

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m\omega^2}{2}x^2 \right] \psi(x, t) = E\psi(x, t), \quad (4.2)$$

with solutions of the form

$$\psi(x, t) = \psi(x)e^{-\frac{i}{\hbar}Et}, \quad (4.3)$$

where $\psi(x)$ is solution of the eigenvalue equation

$$\hat{H}\psi(x) = E\psi(x). \quad (4.4)$$

There are several methods to solve this eigenvalue equation. We will introduce here new operators which allow us to bring the Hamilton operator in a simple (diagonalized) form. It is then easy to write the eigenenergies and the corresponding eigenfunctions.

We define the following linear combinations of position and momentum operator:

$$\hat{a} = \frac{\omega m \hat{x} + i \hat{p}}{\sqrt{2\omega m \hbar}}, \quad (4.5)$$

$$\hat{a}^\dagger = \frac{\omega m \hat{x} - i \hat{p}}{\sqrt{2\omega m \hbar}}, \quad (4.6)$$

where \hat{a} is a non-Hermitian operator, to which it is not possible to assign an observable. This transformation can be inverted:

$$\hat{x} = \sqrt{\frac{\hbar}{2\omega m}} (\hat{a} + \hat{a}^\dagger), \quad (4.7)$$

$$\hat{p} = -i\sqrt{\frac{\hbar\omega m}{2}} (\hat{a} - \hat{a}^\dagger). \quad (4.8)$$

With the commutation relation for position and momentum operator, $[\hat{x}, \hat{p}] = i\hbar$, it follows that

$$[\hat{a}, \hat{a}^\dagger] = 1 \quad \text{and} \quad [\hat{a}^\dagger, \hat{a}] = [\hat{a}, \hat{a}] = 0. \quad (4.9)$$

As we will see in Quantum Mechanics II, these commutation rules for \hat{a} and \hat{a}^\dagger are a property of bosonic degrees of freedom.

We insert now (4.7) and (4.8) in the Hamilton operator (4.1) and we get

$$\hat{H} = \frac{\hbar\omega}{2} (\hat{a}^\dagger \hat{a} + \hat{a} \hat{a}^\dagger) = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right). \quad (4.10)$$

For the last step we used the commutation relation $[\hat{a}, \hat{a}^\dagger] = 1$. The operator

$$\hat{n} = \hat{a}^\dagger \hat{a} \quad (4.11)$$

is Hermitian (therefore it belongs to an observable) and is called occupation number operator. The Hamilton operator is then simply

$$\hat{H} = \hbar\omega \left(\hat{n} + \frac{1}{2} \right), \quad (4.12)$$

i.e., the eigenstates of \hat{n} and of \hat{H} are the same.

We introduce now the (normalized) eigenstates $|\psi_n\rangle$ of \hat{n} :

$$\hat{n}|\psi_n\rangle = n|\psi_n\rangle, \quad (4.13)$$

where for the eigenvalue n it must hold:

$$n = \langle \psi_n | \hat{n} | \psi_n \rangle = \langle \psi_n | \hat{a}^\dagger \hat{a} | \psi_n \rangle = \langle \alpha_n | \alpha_n \rangle \geq 0, \quad (4.14)$$

with $|\alpha_n\rangle = \hat{a}|\psi_n\rangle$. Thus the lowest possible eigenvalue is $n = 0$, defining the *ground state* of the Hamilton operator. (Note that from $\langle\alpha_0|\alpha_0\rangle = 0$ follows $|\alpha_0\rangle = |0\rangle$, the zero element.) The ground state energy is therefore $E_0 = \hbar\omega/2$, again larger than zero because of the Heisenberg's uncertainty principle. The corresponding wave function $\psi_0(x)$ is obtained from the condition

$$0 = \langle x|0\rangle = \langle x|\alpha_0\rangle = \langle x|\hat{a}|\psi_0\rangle = \frac{1}{\sqrt{2}} \left(\frac{x}{x_0} + x_0 \frac{d}{dx} \right) \underbrace{\langle x|\psi_0\rangle}_{\psi_0(x)}, \quad (4.15)$$

where $x_0 = \sqrt{\hbar/\omega m}$ is the characteristic length in this system. The (normalized) solution of this differential equation is

$$\psi_0(x) = \frac{1}{\sqrt{x_0\sqrt{\pi}}} e^{-\frac{x^2}{2x_0^2}}, \quad (4.16)$$

a wave function with the form of a Gaussian function.

The eigenstates with higher energy can be found using the operator relations

$$[\hat{n}, \hat{a}^\dagger] = [\hat{a}^\dagger \hat{a}, \hat{a}^\dagger] = \hat{a}^\dagger [\hat{a}, \hat{a}^\dagger] + [\hat{a}^\dagger, \hat{a}^\dagger] \hat{a} = \hat{a}^\dagger \quad (4.17)$$

and

$$[\hat{n}, \hat{a}] = [\hat{a}^\dagger \hat{a}, \hat{a}] = \hat{a}^\dagger [\hat{a}, \hat{a}] + [\hat{a}^\dagger, \hat{a}] \hat{a} = -\hat{a}. \quad (4.18)$$

From these follow namely

$$\hat{n} \hat{a}^\dagger |\psi_{n-1}\rangle = \hat{a}^\dagger (\hat{n} + 1) |\psi_{n-1}\rangle = n \hat{a}^\dagger |\psi_{n-1}\rangle, \quad (4.19)$$

from which we see that the state $\hat{a}^\dagger |\psi_{n-1}\rangle$ is also an eigenstate of \hat{n} , with eigenvalue n . The norm of $\hat{a}^\dagger |\psi_{n-1}\rangle$ is

$$\sqrt{\langle \psi_{n-1} | \hat{a} \hat{a}^\dagger | \psi_{n-1} \rangle} = \sqrt{\langle \psi_{n-1} | \hat{a}^\dagger \hat{a} + 1 | \psi_{n-1} \rangle} = \sqrt{n}, \quad (4.20)$$

and therefore

$$\hat{a}^\dagger |\psi_{n-1}\rangle = \sqrt{n} |\psi_n\rangle. \quad (4.21)$$

Analogously one finds

$$\hat{a} |\psi_n\rangle = \sqrt{n} |\psi_{n-1}\rangle. \quad (4.22)$$

Since the ground state is defined by $n = 0$, all eigenstates with higher energy (the excited states) can be defined by the relation

$$|\psi_n\rangle = \frac{1}{\sqrt{n!}} (\hat{a}^\dagger)^n |\psi_0\rangle, \quad n = 0, 1, 2, \dots \quad (4.23)$$

They have the eigenenergies

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right). \quad (4.24)$$

The eigenstates $|\psi_n\rangle$ with $n = 0, 1, 2, 3, \dots$ form an orthonormal basis.

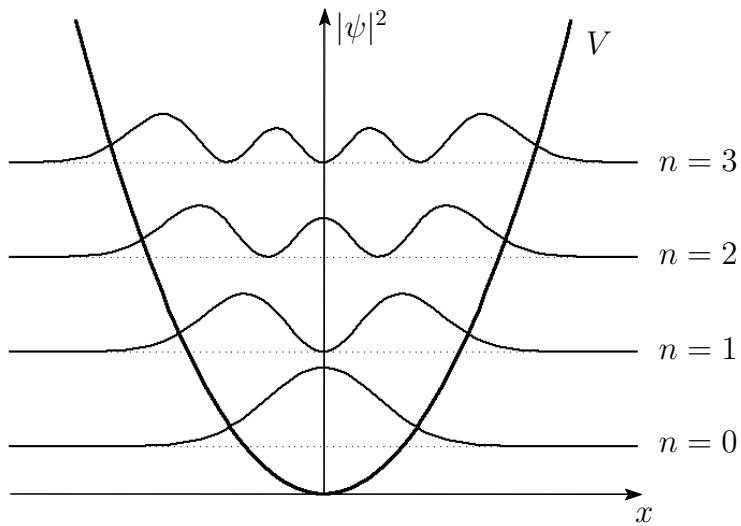


Figure 4.1: Probability density for the 4 lowest energy-eigenstates of the harmonic oscillator.

The wave functions of these states (fig. 4.1) are given by

$$\begin{aligned}\langle x | \psi_n \rangle &= \frac{1}{\sqrt{n!}} \langle x | (\hat{a}^\dagger)^n | \psi_0 \rangle \\ &= \frac{1}{\sqrt{n!}} \left(\frac{x}{x_0} - x_0 \frac{d}{dx} \right)^n \psi_0(x) \\ &= \frac{1}{(2^n n! x_0 \sqrt{\pi})^{1/2}} H_n \left(\frac{x}{x_0} \right) e^{-\frac{x^2}{2x_0^2}},\end{aligned}\quad (4.25)$$

where $H_n(x)$ denote the so-called Hermite polynomials, which are defined as follows:

$$H_n(x) = e^{\frac{x^2}{2}} \left(x - \frac{d}{dx} \right)^n e^{-\frac{x^2}{2}} = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}. \quad (4.26)$$

The first Hermite polynomials are:

$$H_0(x) = 1, \quad H_1(x) = 2x, \quad H_2(x) = 4x^2 - 2, \quad H_3(x) = 8x^3 - 12x, \dots \quad (4.27)$$

The operators \hat{a}^\dagger and \hat{a} are called “creation” and “annihilation” operators, respectively, since if they are applied to an energy eigenstate, it results a state with a higher or with a lower quantum number n , respectively. While \hat{n} commutes with \hat{H} , the following applies (as in (4.17) and (4.18))

$$[\hat{H}, \hat{a}] = -\hbar\omega \hat{a} \quad \text{und} \quad [\hat{H}, \hat{a}^\dagger] = \hbar\omega \hat{a}^\dagger, \quad (4.28)$$

i.e. the energy eigenstates can obviously be neither eigenstates of \hat{a} nor of \hat{a}^\dagger . However, we now want to define eigenstates $|\phi_\alpha\rangle$ of \hat{a} , which of course cannot be stationary states:

$$\hat{a}|\phi_\alpha\rangle = \alpha|\phi_\alpha\rangle, \quad (4.29)$$

where the eigenvalue α is a complex number, $\alpha = |\alpha|e^{i\delta}$. Since $\{|\psi_n\rangle\}$ is an orthonormal basis, we can express the state $|\phi_\alpha\rangle$ in this basis: $|\phi_\alpha\rangle = \sum_n |\psi_n\rangle \langle \psi_n| \phi_\alpha\rangle$, where

$$\langle \psi_n | \phi_\alpha \rangle = \frac{1}{\sqrt{n!}} \langle \psi_0 | \hat{a}^n | \phi_\alpha \rangle = \frac{\alpha^n}{\sqrt{n!}} \langle \psi_0 | \phi_\alpha \rangle. \quad (4.30)$$

It follows

$$|\phi_\alpha\rangle = \langle \psi_0 | \phi_\alpha \rangle \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |\psi_n\rangle. \quad (4.31)$$

The normalization is given by

$$\begin{aligned} 1 &= \langle \phi_\alpha | \phi_\alpha \rangle = |\langle \psi_0 | \phi_\alpha \rangle|^2 \sum_{n,m=0}^{\infty} \frac{\alpha^{*m} \alpha^n}{\sqrt{n! m!}} \underbrace{\langle \psi_m | \psi_n \rangle}_{\delta_{mn}} = \\ &= |\langle \psi_0 | \phi_\alpha \rangle|^2 \sum_{n=0}^{\infty} \frac{|\alpha|^{2n}}{n!} = |\langle \psi_0 | \phi_\alpha \rangle|^2 e^{|\alpha|^2}, \end{aligned} \quad (4.32)$$

i.e., $\langle \psi_0 | \phi_\alpha \rangle = e^{-|\alpha|^2/2}$, and we get:

$$|\phi_\alpha\rangle = e^{-\frac{|\alpha|^2}{2}} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |\psi_n\rangle. \quad (4.33)$$

This state is called a *coherent state*. It is no longer an eigenstate of the occupation number operator \hat{n} , but a coherent superposition of many states with different eigenvalues of \hat{n} . If we consider the expectation value of \hat{n} and the squared standard deviation $\Delta n^2 = \langle (\hat{n} - \langle \hat{n} \rangle)^2 \rangle = \langle \hat{n}^2 \rangle - \langle \hat{n} \rangle^2$, then we obtain

$$\begin{aligned} \langle \hat{n} \rangle &= \langle \phi_\alpha | \hat{n} | \phi_\alpha \rangle = e^{-|\alpha|^2} \sum_{n=0}^{\infty} \frac{n |\alpha|^{2n}}{n!} = \\ &= e^{-|\alpha|^2} \sum_{n=1}^{\infty} \frac{(|\alpha|^2)^n}{(n-1)!} = e^{-|\alpha|^2} |\alpha|^2 \underbrace{\sum_{m=0}^{\infty} \frac{(|\alpha|^2)^m}{m!}}_{e^{|\alpha|^2}} = |\alpha|^2 \end{aligned} \quad (4.34)$$

and

$$\begin{aligned} \Delta n^2 &= e^{-|\alpha|^2} \sum_{n=0}^{\infty} \frac{n^2 |\alpha|^{2n}}{n!} - |\alpha|^4 \\ &= e^{-|\alpha|^2} |\alpha|^2 \sum_{m=0}^{\infty} (m+1) \frac{(|\alpha|^2)^m}{m!} - |\alpha|^4 \\ &= |\alpha|^2 (|\alpha|^2 + 1) - |\alpha|^4 \\ &= |\alpha|^2. \end{aligned} \quad (4.35)$$

It follows that the expectation value of the energy is $\langle E \rangle = \hbar\omega(|\alpha|^2 + 1/2)$ and the deviation is $\Delta E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2} = \hbar\omega|\alpha|$, i.e., $\Delta E/\langle E \rangle \propto \langle E \rangle^{-1/2}$: the higher

the average energy, the smaller the relative deviation (in accordance with Bohr's correspondence principle).

The time evolution of the coherent state is obtained from the time evolution of the stationary states $|\psi_n\rangle$:

$$|\psi_n(t)\rangle = e^{-\frac{i}{\hbar}\hat{H}t}|\psi_n(0)\rangle = e^{-i\omega t(n+1/2)}|\psi_n(0)\rangle, \quad (4.36)$$

from which it follows that

$$|\phi_\alpha(t)\rangle = e^{-i\omega t/2}|\phi_{\alpha(t)}\rangle, \quad \text{with } \alpha(t) = \alpha e^{-i\omega t}. \quad (4.37)$$

Therefore the expectation value of the position operator is

$$\begin{aligned} \langle \hat{x}(t) \rangle &= \langle \phi_\alpha(t) | \hat{x} | \phi_\alpha(t) \rangle \\ &= \frac{x_0}{\sqrt{2}} \langle \phi_{\alpha(t)} | \hat{a} + \hat{a}^\dagger | \phi_{\alpha(t)} \rangle \\ &= \frac{x_0}{\sqrt{2}} (\alpha(t) + \alpha(t)^*) \\ &= \sqrt{2}x_0 |\alpha| \cos(\omega t - \delta), \end{aligned} \quad (4.38)$$

where $\alpha = |\alpha|e^{i\delta}$. This is the time evolution of a classical oscillator. Indeed, we can easily see from the above expression for the expectation value of energy that (for large $|\alpha|$) $\sqrt{2}x_0|\alpha|$ corresponds to the classical oscillation amplitude. Here again we see the correspondence principle in action. Furthermore, in this case, Ehrenfest's theorem corresponds to the Newton's equation of motion.

4.2 Potential step

From now on, we consider a series of piecewise constant potentials in one dimension. First a potential step: $V(x) = V_0\Theta(x)$ with $V_0 > 0$ and $\Theta(x)$ the step function:

$$\Theta(x) = \begin{cases} 0, & x < 0 \\ 1, & x \geq 0 \end{cases}, \quad (4.39)$$

where the step is at $x = 0$ (Fig. 4.2).

The Schrödinger equation can then be written separately for the two sides of the step, where we are again interested in the stationary solutions $\psi(x)$,

$$\begin{aligned} \frac{d^2\psi}{dx^2} &= -\frac{2mE}{\hbar^2}\psi = -k^2\psi, & x < 0 \\ \frac{d^2\psi}{dx^2} &= -\frac{2m(E - V_0)}{\hbar^2}\psi = -q^2\psi, & x \geq 0 \end{aligned} \quad (4.40)$$

where we defined $k = \sqrt{2mE/\hbar}$ and $q = \sqrt{2m(E - V_0)/\hbar}$.

For a finite potential $V(x)$, the wave function ψ and its first derivative ψ' must be continuous everywhere. For the step potential, this must be the case in particular

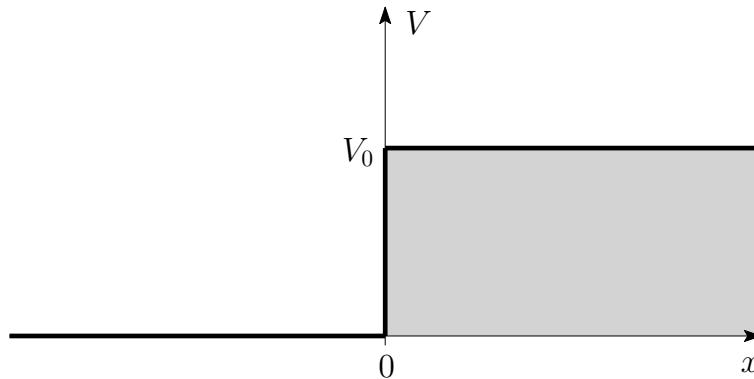


Figure 4.2: Step potential.

at $x = 0$. To understand this fact, we consider an arbitrary point x_0 and integrate the time-independent Schrödinger equation from $x_0 - \epsilon$ to $x_0 + \epsilon$. Then we take the limit $\epsilon \rightarrow 0$:

$$-\frac{\hbar^2}{2m} \underbrace{\int_{x_0-\epsilon}^{x_0+\epsilon} dx \frac{d^2\psi}{dx^2}}_{\psi'(x_0+\epsilon)-\psi'(x_0-\epsilon)} + \underbrace{\int_{x_0-\epsilon}^{x_0+\epsilon} dx V(x)\psi(x)}_{\rightarrow 0 \text{ for } |V|<\infty} = E \underbrace{\int_{x_0-\epsilon}^{x_0+\epsilon} dx \psi(x)}_{\rightarrow 0}. \quad (4.41)$$

Since ψ is bounded and the length of the interval over which we integrate tends to 0, the second term and the right-hand side vanish. Therefore the first term must also be zero, which means that ψ' is continuous in x_0 . However, this is only true if $V(x)$ is bounded. In the infinite potential well this was not the case, therefore ψ was continuous, but ψ' was not.

The solution of the Schrödinger equation (4.40) can obviously be expressed piecewise by plane waves,

$$\psi(x) \sim \begin{cases} e^{\pm ikx}, & x < 0 \\ e^{\pm iqx}, & x \geq 0 \end{cases}. \quad (4.42)$$

We consider two cases:

$E > V_0$: The two momentum parameters k and q in (4.40) are real and we actually find plane waves in both domains. We now consider the situation of a particle coming from $x = -\infty$, which with a certain probability continues to $x = +\infty$ or is reflected back to $x = -\infty$. The Ansatz is

$$\psi(x) = \begin{cases} e^{ikx} + Re^{-ikx}, & x < 0 \\ Te^{iqx}, & x \geq 0 \end{cases}, \quad (4.43)$$

where e^{ikx} represents the incident, Re^{-ikx} the reflected and Te^{iqx} the transmitted wave. The two continuity conditions at $x = 0$ gives the amplitudes R and T as

function of the energy,

$$\left. \begin{array}{l} 1 + R = T \\ ik(1 - R) = iqT \end{array} \right\} \Rightarrow \left\{ \begin{array}{l} R = \frac{k - q}{k + q} = \frac{\sqrt{E} - \sqrt{E - V_0}}{\sqrt{E} + \sqrt{E - V_0}} \\ T = \frac{2k}{k + q} = \frac{2\sqrt{E}}{\sqrt{E} + \sqrt{E - V_0}} \end{array} \right. . \quad (4.44)$$

Notice that $R > 0$ for $V_0 > 0$; for $V_0 < 0$, i.e., for a step downwards, it would be $R < 0$, which corresponds to a phase shift by π .

From the continuity equation (2.54) it follows that for stationary states ($\frac{\partial \rho}{\partial t} = 0$) in one dimension, the probability current density (2.55) is necessarily a constant, i.e., it is equal for $x < 0$ and $x > 0$. From (4.43) the probability current density is:

$$J_{x<0} = \frac{\hbar k}{m}(1 - |R|^2) = J_0 - J_r, \quad (4.45)$$

$$J_{x>0} = \frac{\hbar q}{m}|T|^2 = J_t, \quad (4.46)$$

where J_0 is the incident, J_r the reflected and J_t the transmitted probability current density. The equality $J_{x<0} = J_{x>0}$ gives the following relation between R and T :

$$k(1 - |R|^2) = q|T|^2. \quad (4.47)$$

One can easily check that it is satisfied by the amplitudes in (4.44).

The probability that the particle is reflected, or respectively transmitted, at the step, is defined by

$$r = \frac{J_r}{J_0} = |R|^2 \quad \text{and} \quad t = \frac{J_t}{J_0} = \frac{q}{k}|T|^2. \quad (4.48)$$

Here obviously $1 - r = t$ holds. In contrast to classical physics the quantum mechanical particle can be reflected even if the energy is higher than the step.

$0 < E < V_0$: Under this condition $q = i\sqrt{2m(V_0 - E)}/\hbar = i\kappa$ becomes purely imaginary and the wave function in the region $x > 0$ has exponentially increasing or decreasing solutions. However, only the decreasing solution is physically relevant, because of the normalizability condition of the wave function,

$$\psi(x) = Te^{-\kappa x}, \quad \text{for } x > 0, \quad (4.49)$$

where $\kappa = -iq$. From this follows that $J_{x>0} = 0$ and therefore also $J_{x<0} = 0$. Thus we find $|R|^2 = 1$, i.e., total reflection, as in the classical case. The wave function in the “forbidden” region decreases exponentially, so the probability to find the particle for $x \rightarrow \infty$ vanishes. Since $|R| = 1$, one can represent R by a phase, $R = -e^{2i\delta(E)}$ with

$$\delta(E) = \arccot\left(\frac{\kappa}{k}\right), \quad ? \quad (4.50)$$

as can be obtained from (4.44). The phase δ represents the phase shift of the particle wave function because of the reflection.

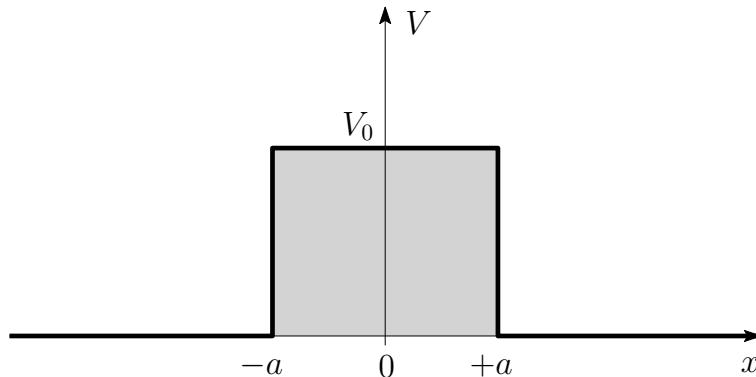


Figure 4.3: Potential barrier.

4.3 Potential barrier

We consider now a potential barrier of the form $V(x) = V_0\Theta(a - |x|)$, where we focus on the case $0 < E < V_0$. The regions $a < |x| < \infty$ are here identical (fig. 4.3).

A particle, coming from $x = -\infty$, scatters at this potential barrier. The wave function can be written piecewise in the three regions:

$$\psi(x) = \begin{cases} Ae^{ik(x+a)} + Be^{-ik(x+a)}, & x < -a \\ Ce^{-\kappa x} + De^{\kappa x}, & -a \leq x \leq +a \\ AS(E)e^{ik(x-a)}, & +a < x \end{cases} \quad (4.51)$$

where $k = \sqrt{2mE/\hbar}$ and $\kappa = \sqrt{2m(V_0 - E)/\hbar}$. This solution must satisfy the continuity conditions at $x = -a$ and $x = +a$. Without giving the details of the calculation here, we give the result for $S(E)$:

$$S(E) = \frac{2ik\kappa}{2ik\kappa \cosh(2\kappa a) + (k^2 - \kappa^2) \sinh(2\kappa a)}. \quad (4.52)$$

This results in a finite transmission probability:

Tunneling effect?

$$t(E) = |S(E)|^2 = \left[1 + \frac{\sinh^2(2\kappa a)}{4(E/V_0)(1 - E/V_0)} \right]^{-1}, \quad (4.53)$$

i.e. even if the energy of a particle is smaller than the potential of the barrier, it can traverse the barrier with a finite probability. This *tunnel effect* is a typical quantum effect, because it is not possible classically. This can be understood with the fact that the particle is in the region of the barrier only for a limited amount of time. Therefore, due to the energy-time uncertainty relation, the true energy of the particle cannot be determined during the tunneling process. Such tunneling phenomena occur in decay processes like the α decay of a nucleus. The α particle is bound to the nucleus by a potential barrier, but it can decay with a certain probability (which defines the decay rate). In semiconductor technology and spectroscopy there are also tunnel contacts, where conduction electrons tunnel from one system to another. The tunneling probability defines the electrical resistance of the contact (fig. 4.4).

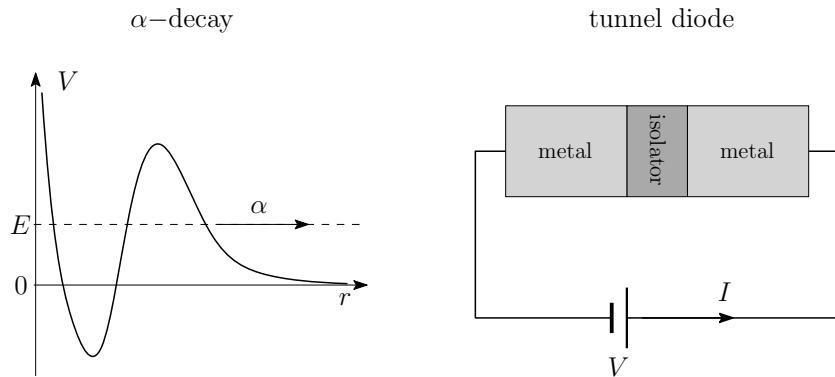


Figure 4.4: On the left hand-side the potential of a nucleus in an α -decay; on the right-hand side the structure of a tunnel diode.

An important aspect of the tunneling probability $t(E)$ in (4.53) is the exponential dependence on the barrier width $2a$ (for $\kappa a \gg 1$):

$$t(E) \approx 16 \frac{E}{V_0} \left(1 - \frac{E}{V_0}\right) e^{-4\kappa a}. \quad (4.54)$$

This very strong dependence of the tunneling effect on a is the basis for a very important instrument in surface investigation and spectroscopy, the scanning tunneling microscope (STM), which allows to obtain high resolution images of metal surfaces by using the tunneling effect. Electrons tunnel out of an extremely fine metal tip, which is only a few Ångström away from the metallic surface. The tip scans over the surface, and the current strength gives then information about the distance, i.e., the structure of the surface. This method provides in many cases images with atomic resolution (fig. 4.5). In addition one can also obtain information about local electron states¹.

¹This microscope was developed in the late 1970s by Heinrich Rohrer and Gerd Binnig at the IBM research laboratory in Rüschlikon (Nobel Prize 1986; Review of Modern Physics **59**, 615 (1987)).



Figure 4.5: Scanning tunneling microscope: on the left-hand side the setup, on the right-hand side the picture obtained for a graphite surface.

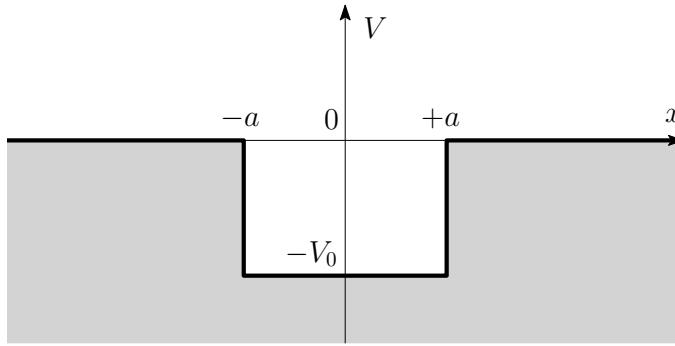


Figure 4.6: A finite potential well.

4.4 Potential well

Next we turn to the potential $V(x) = -V_0\Theta(a - |x|)$ (with $V_0 > 0$), i.e. the region $-a < x < +a$ has a lower potential (fig. 4.6). As characteristic properties of this potential well we find bound states (for $E < 0$) and scattering states (with transmission resonances, for $E > 0$). The energy spectrum has both a discrete and a continuous part. We first investigate the bound states, whose wave functions are concentrated in the region of the well and decrease exponentially with distance.

$-V_0 < E < 0$: In this energy range, the wave function has the form

$$\psi(x) = \begin{cases} Ae^{\kappa(x+a)}, & x < -a \\ Be^{ikx} + Ce^{-ikx}, & -a \leq x \leq +a \\ De^{-\kappa(x-a)}, & +a < x \end{cases} \quad (4.55)$$

where $k = \sqrt{2m(E + V_0)/\hbar}$ and $\kappa = \sqrt{-2mE/\hbar}$. The continuity conditions at $x = \pm a$ give for ψ

$$A = Be^{-ika} + Ce^{ika} \quad \text{and} \quad D = Be^{ika} + Ce^{-ika}, \quad (4.56)$$

and for ψ'

$$\kappa A = ik(Be^{-ika} - Ce^{ika}) \quad \text{and} \quad \kappa D = -ik(Be^{ika} - Ce^{-ika}). \quad (4.57)$$

We use the symmetry of the potential under parity ($x \leftrightarrow -x$) to classify the solutions of the time-independent Schrödinger equation in even and odd wavefunctions, respectively,² as we did for the infinite potential well.

For the states with even parity ($\psi(-x) = +\psi(x)$), the relations $A = D$ and $B = C$ hold. Then the continuity conditions can be summarized by the equation

$$1 = \frac{k}{\kappa} \tan(ka) \Rightarrow \frac{\sqrt{\chi^2 - (ka)^2}}{ka} = \tan(ka), \quad (4.58)$$

where $\chi = a\sqrt{2mV_0/\hbar}$. In the same manner, for the states with odd parity ($\psi(-x) = -\psi(x)$), from $A = -D$ and $B = -C$ we get

$$1 = -\frac{k}{\kappa} \cot(ka) \Rightarrow \frac{\sqrt{\chi^2 - (ka)^2}}{ka} = -\cot(ka). \quad (4.59)$$

²In chapter 6 we will describe this procedure and the connection between symmetries and conservation laws more generally.

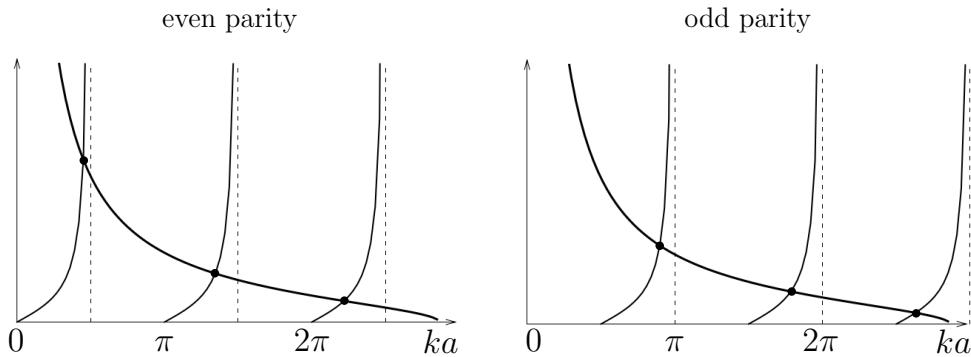


Figure 4.7: Graphic solution of equations (4.58) and (4.59). On the right-hand side for even parity, on the right-hand side for odd parity. The black dots mark the solutions.

Both equations can only be satisfied by a discrete set of energy values. They are transcendental numbers and can only be solved numerically or graphically, as shown in Fig. 4.7.

The ground state (corresponding to the lowest k value) has even parity. The following wave functions correspond, in an alternating way, to eigenstates with odd and even parity. Furthermore, it can be seen that the wave function of the ground state has no nodal point. With increasing energy the number of nodes increases each time by one, so that the states can be numbered sequentially according to the number of their nodes (fig. 4.8). The eigenstates of the infinite potential well and of the harmonic oscillator showed the same behavior.

The number of bound states depends on the width, $2a$, and the depth, $-V_0$, of the potential well. In one dimension, however, there is always at least one bound state (with even parity) in the symmetric potential well, as can be easily seen from Fig. (4.7): the first branch of the tangent function is always cut and yields a solution.

$E > 0$: There are no bound states for positive energies. Similar to the potential barrier, we study the scattering of a particle incident from the left. For this reason we make here the following Ansatz for the wave function:

$$\psi(x) = \begin{cases} Ae^{ik(x+a)} + Be^{-ik(x+a)}, & x < -a \\ Ce^{iqx} + De^{-iqx}, & -a \leq x \leq +a \\ AS(E)e^{ik(x-a)}, & +a < x \end{cases} \quad (4.60)$$

with $k = \sqrt{2mE}/\hbar$ and $q = \sqrt{2m(E + V_0)}/\hbar$. The continuity conditions give the transmission amplitude,

$$S(E) = \frac{2kq}{2kq \cos(2qa) - i(k^2 + q^2) \sin(2qa)}, \quad (4.61)$$

and the transmission probability as function of the energy E :

$$t(E) = |S(E)|^2 = \left[1 + \frac{\sin^2(2qa)}{4(E/V_0)(1 + E/V_0)} \right]^{-1}. \quad (4.62)$$

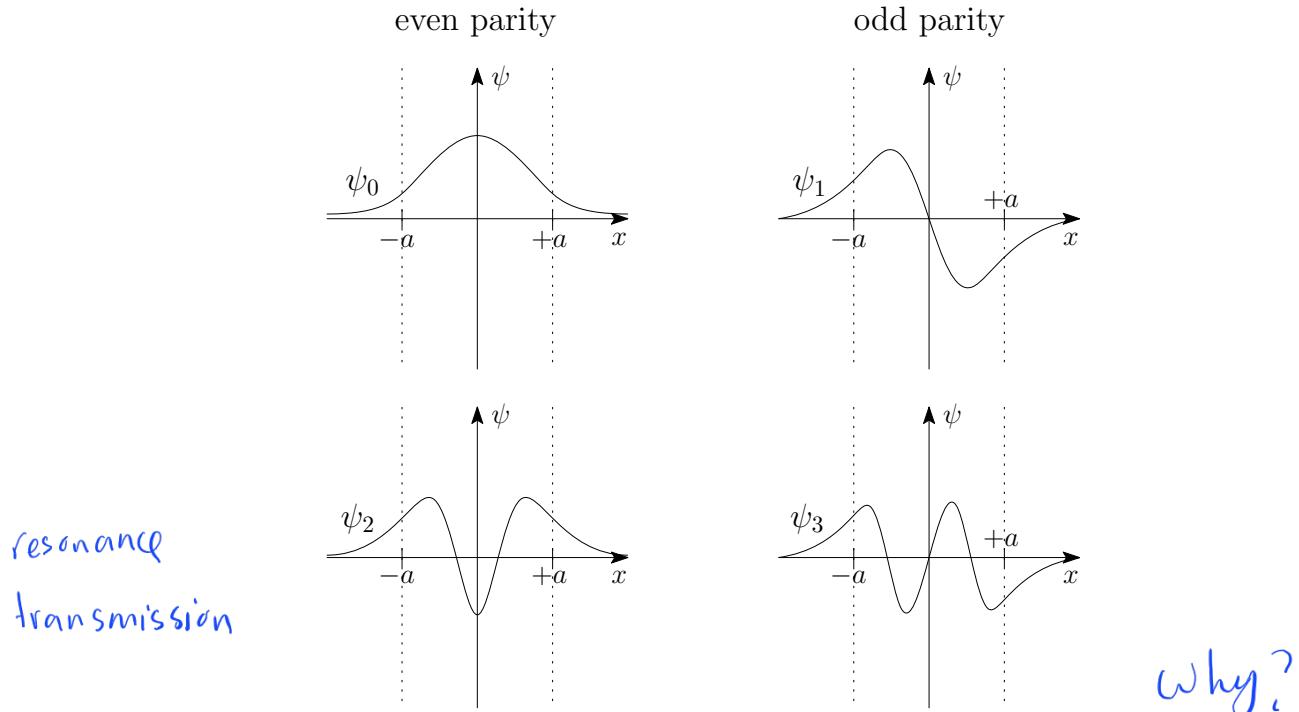


Figure 4.8: Wave functions with even and odd parity for the finite potential well: the ground state ψ_0 is even, the first excited state ψ_1 is odd, the second excited state ψ_2 is again even and so on, with increasing energy.

From this equation it follows that $t(E)$ is equal to 1 only at very specific energy values, corresponding to $\sin(2qa) = 0$, i.e. $2qa = n\pi$. These energies are therefore given by $E_n = (\hbar\pi n)^2/8ma^2 - V_0$, where $n \geq n_{\min}$ with $E_{n_{\min}} > 0$. These energies with perfect transmission correspond to resonances. They can be understood as interference effect of the two reflected waves. One coming from $x = -a$ with phase factor $e^{i\pi}$ and the other from $x = +a$ with e^{i0} . Thus, one obtains complete destructive interference for the reflected wave when $4qa = 2\pi n$, because of the difference π in the phase shift: in this case there is no reflection and the particle is transmitted with probability 1 (Fig. 4.9). Alternatively, resonance can be thought of as a “virtually bound” state. This arises from the reflection of the particle at the walls of the well (note: a quantum mechanical effect for $E > 0$, as seen in (4.2)), which then remains trapped in the well region for some time. This is the result of constructive interference for the multiple reflected wave (as for standing waves).

We now focus on $S(E)$ in the vicinity of a resonance. In the vicinity of the energy E_n we can linearize the denominator and express $S(E)$ as

$$S(E) \approx \frac{1}{\cos(\pi n)} \frac{i\Gamma/2}{E - E_n + i\Gamma/2}, \quad (4.63)$$

where

$$\frac{1}{\Gamma} = \frac{a}{2} \left[\frac{k^2 + q^2}{qk} \frac{dq}{dE} \right]_{E=E_n} = \frac{\chi}{4} \frac{1 + 2E_n/V_0}{V_0 \sqrt{E_n/V_0} (1 + E_n/V_0)}, \quad (4.64)$$

with the dimensionless parameter $\chi = a\sqrt{2mV_0/\hbar}$. Here $S(E)$ has the form of a

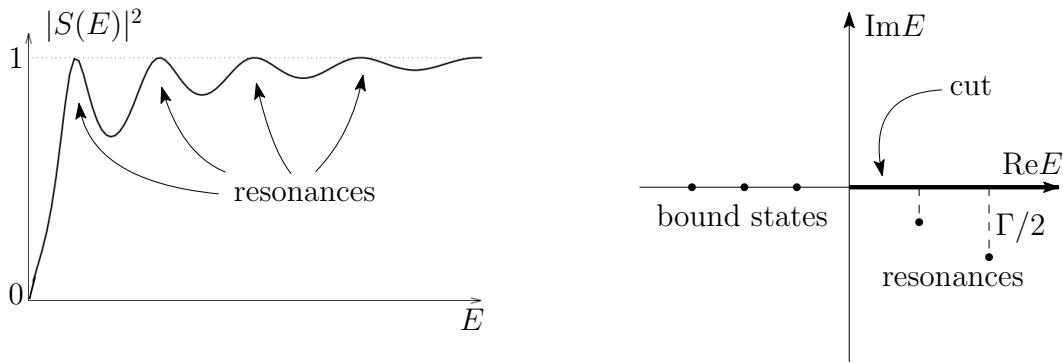


Figure 4.9: On the left-hand side: $|S(E)|^2$ as function of E . On the right-hand side: the poles of $S(E)$ in the complex plane correspond to bound states or resonances.

Lorentz function, which is often called a Breit-Wigner function in the context of resonances. Γ corresponds to the width of the resonance. Obviously resonances become broader at higher energies E_n , whereas deeper potentials have narrower resonances. The width of the resonance can also be related to the decay rate of the virtual bound state, by means of the uncertainty relation $\Delta E \Delta t \gtrsim \hbar$: $1/\Delta t \approx \Gamma/\hbar$.

The phase shift $\delta(E)$ of the wave function for transmission is defined by $S(E) = \sqrt{t(E)} e^{i\delta(E)}$, which gives

$$\tan(\delta(E)) = \frac{1}{2} \left(\frac{k^2 + q^2}{qk} \right) \tan(2qa). \quad (4.65)$$

In the vicinity of a resonance, we get approximately

$$\tan(\delta(E)) \approx \frac{2}{\Gamma}(E - E_n). \quad (4.66)$$

At a certain distance from the resonance δ approaches the values $\pm\pi/2$. But near to the resonance δ goes relatively quickly through 0 or π .

If we analyze $S(E)$ more generally, we can extend E to be a complex variable and study the behavior of $S(E)$ in the complex plane. Because of the roots \sqrt{E} , the analytic extension of $S(E)$ involves both Riemann sheets and has a cut along the positive real axis (Fig. 4.9). $S(E)$ now has poles on the second Riemann sheet at $E = E_n - i\Gamma/2$, which correspond to the transmission resonances. However, the analytic extension also yields poles on the first Riemann sheet on the negative real axis. These poles correspond to the bound states of the potential well. One can indeed show that the poles of $S(E)$ with $E < 0$ satisfy the equations (4.58) or (4.59).

4.5 δ potential

potential well vs potential barrier

A special case of a potential well ($V_0 < 0$) or a potential barrier ($V_0 > 0$) is the δ potential $V(x) = V_0\delta(x)$, which is localized at $x = 0$. The time independent Schrödinger equation is

$$\left(\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + E \right) \psi(x) = V_0 \delta(x) \psi(x). \quad (4.67)$$

We integrate both sides of the equation from $-\varepsilon$ to $+\varepsilon$ (with $\varepsilon > 0$) and let $\varepsilon \rightarrow 0$:

$$\frac{\hbar^2}{2m} \left(\frac{d}{dx} \psi(x) \Big|_{x=0_+} - \frac{d}{dx} \psi(x) \Big|_{x=0_-} \right) = V_0 \psi(0), \quad (4.68)$$

i.e., while the wave function is continuous everywhere, the delta potential produces a discontinuity in its derivative. Again we can calculate the transmission probability for $E > 0$ with the Ansatz

$$\psi(x) = \begin{cases} e^{ikx} + Re^{-ikx}, & x < 0, \\ S(E)e^{ikx}, & x > 0, \end{cases} \quad (4.69)$$

where $k = \sqrt{2mE}/\hbar$. From the continuity of ψ and from (4.68) we get $1 + R = S(E)$ and $-ik\hbar^2(1 - R - S(E)) = 2mS(E)V_0$, so that

$$S(E) = \frac{-ik\hbar^2}{mV_0 - ik\hbar^2} = \frac{-i\hbar\sqrt{2mE}}{mV_0 - i\hbar\sqrt{2mE}}. \quad (4.70)$$

The transmission probability and the phase shift are then:

$$t(E) = |S(E)|^2 = \frac{2mE\hbar^2}{m^2V_0^2 + 2mE\hbar^2}, \quad (4.71)$$

$$\delta(E) = -\arctan\left(\frac{mV_0}{\hbar\sqrt{2mE}}\right). \quad \text{resonance} \quad (4.72)$$

We note that there are no resonances for positive as well as for negative V_0 .

For the negative (attractive) potential there is exactly one bound state. Since the energy has to be negative, the wave function decreases exponentially on both sides of the δ potential:

$$\psi(x) = Ae^{-\kappa|x|}, \quad (4.73)$$

with $\kappa = \sqrt{-2mE}/\hbar$. With (4.68) we get the equation, which allows to determine the energy:

$$-\frac{\hbar^2}{2m}2\kappa A = V_0 A \quad \Rightarrow \quad E = -\frac{mV_0^2}{2\hbar^2}. \quad (4.74)$$

There is only one bound state which has a node-free wave function of even parity.

4.6 Periodic potentials

Bloch wave function / Bloch theorem

An important class of systems are those which have periodic potentials. For example, electrons in a solid are subjected to the potential of periodically arranged atoms (ion-crystal lattice). A periodic potential has the property that it is invariant under a translation by a certain distance a and its multiples, i.e.:

$$V(x) = V(x + a) = V(x + na), \quad (4.75)$$

where n is an integer. We can define a translation operator \hat{T}_a by

$$\hat{T}_a|x\rangle = |x - a\rangle. \quad (4.76)$$

Then it holds

$$\langle x | \hat{T}_a = \langle x + a |, \quad (4.77)$$

so that $\langle x | \hat{T}_a | y \rangle = \langle x | y - a \rangle = \delta(x - y + a) = \langle x + a | y \rangle = \langle x | \hat{T}_a | y \rangle$ is consistent. It also holds that

$$\hat{T}_a | p \rangle = \int dx | x \rangle \langle x + a | p \rangle = \int dx e^{\frac{i}{\hbar} p(x+a)} | x \rangle = e^{\frac{i}{\hbar} pa} \int dx | x \rangle \langle x | p \rangle = e^{\frac{i}{\hbar} pa} | p \rangle, \quad (4.78)$$

from which we get

$$\hat{T}_a = e^{\frac{i}{\hbar} \hat{p} a}, \quad (4.79)$$

i.e., we can represent translations using the momentum operator. \hat{T}_a is a unitary transformation, i.e., $\hat{T}_a^{-1} = \hat{T}_a^\dagger$. The Hamilton operator $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$ is invariant under such translations, so that it commutes with \hat{T}_a : $[\hat{T}_a, \hat{H}] = 0$. It follows that \hat{H} and \hat{T}_a have a common set of eigenstates $|\psi_\lambda\rangle$:

$$\hat{T}_a |\psi_\lambda\rangle = \lambda |\psi_\lambda\rangle, \quad (4.80)$$

from which we get

$$\langle x + na | \psi_\lambda \rangle = \langle x | \hat{T}_a^n | \psi_\lambda \rangle = \lambda^n \langle x | \psi_\lambda \rangle. \quad (4.81)$$

It follows that $|\lambda| = 1$, otherwise the wave function $\psi_\lambda(x) = \langle x | \psi_\lambda \rangle$ for $x \rightarrow +\infty$ or $-\infty$ would either go to 0 or diverge to infinity. This would be incompatible with normalizability and periodicity. Therefore we define $\lambda = e^{ika}$, where the real parameter k is introduced. The wave function of the eigenstate has then the form,

$$\psi(x) = e^{ikx} u_k(x), \quad (4.82)$$

with $u_k(x+a) = u_k(x)$, i.e. $u_k(x)$ is invariant under the translation \hat{T}_a and the action of \hat{T}_a on the wave function is simply given by multiplication with a phase factor. The fact that the wave function has this structure is called **Bloch theorem**. The differential equation which determines the **Bloch wave function** $u_k(x)$ follows from the Schrödinger equation:

$$-\frac{\hbar^2}{2m} \left(\frac{d^2}{dx^2} + 2ik \frac{d}{dx} - k^2 \right) u_k(x) + V(x) u_k(x) = E u_k(x). \quad (4.83)$$

The parameter k is also called **pseudo-momentum**. It holds:

$$\lambda = e^{ika} = e^{i(k+Q)a}, \quad \text{with} \quad Q = \frac{2\pi}{a}, \quad (4.84)$$

i.e., k and $k + Q$ correspond to the same eigenvalue. Therefore we have to consider k only on a finite range $-\frac{\pi}{a} \leq k < +\frac{\pi}{a}$, the so-called **first Brillouin zone**. Q is a so-called reciprocal lattice vector.

The general solution of equation (4.83) is difficult and we will therefore study the exactly solvable **Kronig-Penney model** as an example, given by periodically arranged δ potentials:

$$V(x) = V_0 \sum_{n=-\infty}^{+\infty} \delta(x - na). \quad (4.85)$$

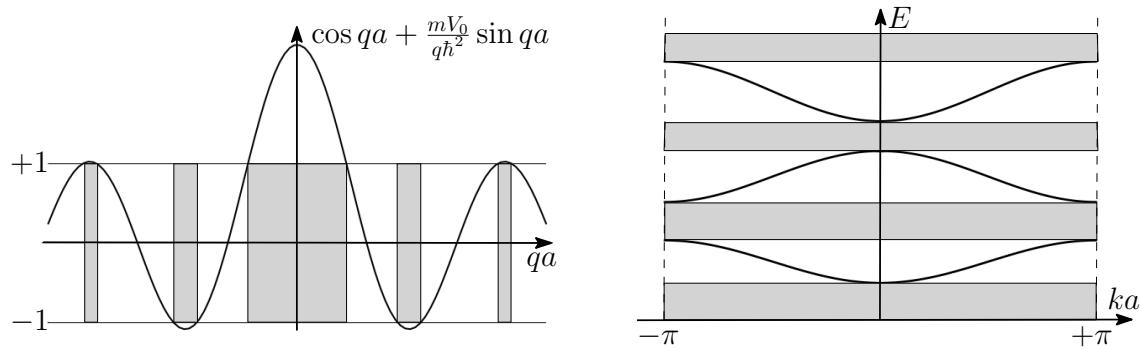


Figure 4.10: On the left-hand side: graphic solution of equation 4.91; the energy intervals without solution, i.e. the gaps, are shaded in grey. On the right-hand side: energy bands and gaps in the first Brillouin zone.

Since between $x = na$ and $x = (n + 1)a$ the potential is constant equal to 0, the wave function for given energy $E > 0$ must correspond again to a plane wave in each such interval,

$$\psi(x) = Ae^{iqx} + Be^{-iqx}, \quad (4.86)$$

with $q = \sqrt{2mE}/\hbar$. The periodic and continuous Bloch wave function is then

$$u_k(x) = Ae^{i(q-k)x} + Be^{-i(q+k)x}, \quad (4.87)$$

with the conditions $u_k(x + a) = u_k(x)$ and $u_k(na + \epsilon) - u_k(na - \epsilon) \rightarrow 0$, for $\epsilon \rightarrow 0$. Furthermore, we integrate the Bloch equation from $-\epsilon$ to $+\epsilon$,

$$\left. \frac{d}{dx} u_k(x) \right|_{x=+\epsilon} - \underbrace{\left. \frac{d}{dx} u_k(x) \right|_{x=-\epsilon}}_{\left. \frac{du_k(x)}{dx} \right|_{x=a-\epsilon}} = \frac{2mV_0}{\hbar^2} u_k(0). \quad (4.88)$$

From the periodicity of u_k and (4.88) we get following conditions:

$$Ae^{i(q-k)a} + Be^{-i(q+k)a} = A + B, \quad (4.89)$$

$$iq(A - B - Ae^{i(q-k)a} + Be^{-i(q+k)a}) = \frac{2mV_0}{\hbar^2}(A + B). \quad (4.90)$$

This system of equations has only for certain values of q and k a non-trivial solution for A and B , resulting in the eigenvalue equation:

$$\cos ka = \cos qa + \frac{mV_0}{q\hbar^2} \sin qa. \quad (4.91)$$

For given ka we can determine qa (e.g. graphically, see Fig. 4.10).

Because of $-1 \leq \cos ka \leq 1$ not all values of qa give allowed energies. The allowed energy intervals belong to bands of states in the periodic potential (white regions in Fig. 4.10). They are separated by energy gaps (gray regions in the figure). The role of the momentum for a free particle is taken here by the pseudo-momentum with $-\frac{\pi}{a} \leq k < \frac{\pi}{a}$. The Bloch states form an important basis for the electron band theory of solids like metals, semiconductors or insulators.

Chapter 5

Central potentials and angular momentum

Central potentials play an important role in physics, e.g. for natural and artificial atoms (quantum dots) or Cooper pairing in superconductors. The angular momentum as a conserved quantity is of outstanding importance in the symmetry classification of states, in the selection rules and in the description of scattering processes.

What's a Hermitian operator?

5.1 The angular momentum

The correspondence principle allows us to convert the classical angular momentum directly into a quantum mechanical operator:

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = \begin{pmatrix} \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \end{pmatrix}. \quad (5.1)$$

This is an observable and thus a Hermitian operator. The commutation rules follow from that of $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$:

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k, \quad (5.2)$$

$$[\hat{L}_i, \hat{r}_j] = i\hbar\epsilon_{ijk}\hat{r}_k, \quad (5.3)$$

$$[\hat{L}_i, \hat{p}_j] = i\hbar\epsilon_{ijk}\hat{p}_k, \quad (5.4)$$

where we sum over repeated indices, and ϵ_{ijk} is the fully antisymmetric tensor,

$$\epsilon_{ijk} = \begin{cases} +1, & \text{even permutation of } (xyz) \\ -1, & \text{odd permutation of } (xyz) \\ 0, & \text{otherwise} \end{cases}, \quad (5.5)$$

i.e., $\epsilon_{ijk}r_i p_j = (\mathbf{r} \times \mathbf{p})_k$. It follows then

$$\hat{\mathbf{L}} \times \hat{\mathbf{L}} = i\hbar\hat{\mathbf{L}}. \quad (5.6)$$

While the angular momentum components do not commute with each other, one finds that $\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ commutes with all components:

$$[\hat{\mathbf{L}}^2, \hat{L}_j] = 0. \quad (5.7)$$

This is important for the discussion of the eigenstates of the angular momentum operator. Since it is obviously not possible to find states which are at the same time eigenstates of all three components, we select one component, e.g. \hat{L}_z , and find its eigenstates which are also eigenstates of $\hat{\mathbf{L}}^2$. The commutation properties now determine the properties of the eigenvalues spectrum.

It is useful to introduce as new operators the following combinations of the angular momentum components orthogonal to \hat{L}_z :

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y, \quad (5.8)$$

with the commutation relations

$$[\hat{L}_z, \hat{L}_{\pm}] = \pm \hbar \hat{L}_{\pm} \quad \text{and} \quad [\hat{L}_+, \hat{L}_-] = 2\hbar \hat{L}_z. \quad (5.9)$$

and with

$$\hat{L}_+ \hat{L}_- = \hat{L}_x^2 + \hat{L}_y^2 - i[\hat{L}_x, \hat{L}_y] = \hat{L}_x^2 + \hat{L}_y^2 + \hbar \hat{L}_z = \hat{\mathbf{L}}^2 + \hbar \hat{L}_z - \hat{L}_z^2, \quad (5.10)$$

$$\hat{L}_- \hat{L}_+ = \hat{\mathbf{L}}^2 - \hbar \hat{L}_z - \hat{L}_z^2. \quad (5.11)$$

We assume now that $|\psi\rangle$ is a normalized eigenstate of \hat{L}_z :

$$\hat{L}_z |\psi\rangle = \lambda |\psi\rangle. \quad (5.12)$$

Then we find that the states $\hat{L}_{\pm} |\psi\rangle$ are also eigenstates of \hat{L}_z :

$$\hat{L}_z \hat{L}_{\pm} |\psi\rangle = \hat{L}_{\pm} \hat{L}_z |\psi\rangle \pm \hbar \hat{L}_{\pm} |\psi\rangle = (\lambda \pm \hbar) \hat{L}_{\pm} |\psi\rangle, \quad (5.13)$$

where \hat{L}_{\pm} increases or decreases the eigenvalue by \hbar . Furthermore, let $|\psi\rangle$ be also eigenstate of $\hat{\mathbf{L}}^2$:

$$\hat{\mathbf{L}}^2 |\psi\rangle = \beta |\psi\rangle. \quad (5.14)$$

Since $[\hat{L}_{\pm}, \hat{\mathbf{L}}^2] = 0$, the eigenstates $\hat{L}_{\pm} |\psi\rangle$ have the same eigenvalue β ,

$$\hat{\mathbf{L}}^2 \hat{L}_{\pm} |\psi\rangle = \hat{L}_{\pm} \hat{\mathbf{L}}^2 |\psi\rangle = \beta \hat{L}_{\pm} |\psi\rangle. \quad (5.15)$$

We compute the squared norm of the states $\hat{L}_{\pm} |\psi\rangle$,

$$\langle \psi | \hat{L}_{\mp} \hat{L}_{\pm} | \psi \rangle = \langle \psi | (\hat{\mathbf{L}}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z) | \psi \rangle = \beta - \lambda^2 \mp \hbar \lambda. \quad (5.16)$$

This squared norm cannot be negative and we get the condition:

$$\beta \geq |\lambda|(|\lambda| + \hbar). \quad (5.17)$$

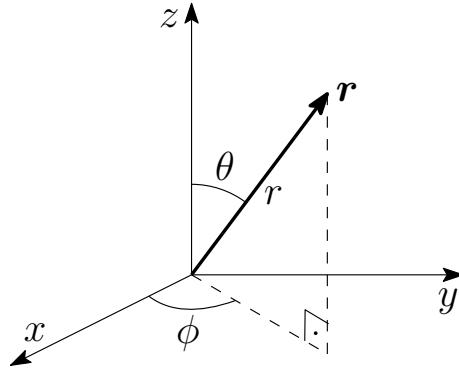


Figure 5.1: Spherical coordinates.

The Ansatz $\beta = \hbar^2 l(l+1)$ and $\lambda = \hbar m$ gives the constraint $|m| \leq l$. Therefore, for a given l there is a state $|\psi_M\rangle$ with a maximal value M for m , so that $\hat{L}_+|\psi_M\rangle = |0\rangle$. From (5.16) it follows immediately that $l(l+1) = M(M+1)$, i.e., $M = l$. In the same way we determine the minimal value to be $M' = -l$. Therefore the eigenvalues are $m = l, l-1, l-2, \dots, -l+1, -l$ and $2l$ must be an integer. It follows that l can be an integer $(0, 1, 2, 3, \dots)$ or a half integer $(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots)$.

From now on the eigenstates are denoted using their quantum numbers with $|l, m\rangle$, so that

$$\hat{\mathbf{L}}^2|l, m\rangle = \hbar^2 l(l+1)|l, m\rangle, \quad (5.18)$$

$$\hat{L}_z|l, m\rangle = \hbar m|l, m\rangle, \quad (5.19)$$

and

$$\hat{L}_{\pm}|l, m\rangle = \hbar\sqrt{l(l+1)-m(m\pm 1)}|l, m\pm 1\rangle. \quad (5.20)$$

The z -axis is called the quantization axis and can be freely chosen in a rotationally symmetric system. In the following we will see that the *orbital angular momentum* takes only integer values l . Half-integer values are reserved for the *spin quantum numbers* (see Chapter 7).

We want now to express the *angular momentum operators* using *spherical coordinates* (Fig. 5.1):

$$\mathbf{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} r \cos \phi \sin \theta \\ r \sin \phi \sin \theta \\ r \cos \theta \end{pmatrix}. \quad (5.21)$$

With the *unit vectors*

$$\mathbf{e}_r = \begin{pmatrix} \cos \phi \sin \theta \\ \sin \phi \sin \theta \\ \cos \theta \end{pmatrix}, \quad \mathbf{e}_{\theta} = \begin{pmatrix} \cos \phi \cos \theta \\ \sin \phi \cos \theta \\ -\sin \theta \end{pmatrix}, \quad \mathbf{e}_{\phi} = \begin{pmatrix} -\sin \phi \\ \cos \phi \\ 0 \end{pmatrix}, \quad (5.22)$$

we have $\mathbf{r} = r\mathbf{e}_r$ and the *derivative* ∇ corresponds to

$$\nabla = \mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \mathbf{e}_{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}. \quad (5.23)$$

With these definitions, after some manipulation it follows:

$$\widehat{L}_x = \frac{\hbar}{i} \left(-\sin \phi \frac{\partial}{\partial \theta} - \cos \phi \cot \theta \frac{\partial}{\partial \phi} \right), \quad (5.24)$$

$$\widehat{L}_y = \frac{\hbar}{i} \left(\cos \phi \frac{\partial}{\partial \theta} - \sin \phi \cot \theta \frac{\partial}{\partial \phi} \right), \quad (5.25)$$

$$\widehat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}. \quad (5.26)$$

Furthermore,

$$\widehat{\mathbf{L}}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]. \quad (5.27)$$

We now search for the wave functions which belong to the eigenstates $|l, m\rangle$. These can be separated into a θ - and a ϕ -dependent part:

$$\langle \theta, \phi | l, m \rangle = \Theta(\theta) \Phi(\phi). \quad (5.28)$$

First we find the differential equation

$$\widehat{L}_z \Phi(\phi) = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \Phi(\phi) \stackrel{!}{=} \hbar m \Phi(\phi) \quad (5.29)$$

with the solution

$$\Phi(\phi) = e^{im\phi}. \quad (5.30)$$

Since the wave function has to be single-valued and continuous, Φ must satisfy the condition $\Phi(\phi + 2\pi) = \Phi(\phi)$, which leads to $e^{i2\pi m} = 1$, so that m (and therefore also l) can only be integer.

From $\widehat{\mathbf{L}}^2 |l, m\rangle = \hbar^2 |l, m\rangle$ we get a differential equation for $\Theta(\theta)$:

$$\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) - \frac{m^2}{\sin^2 \theta} + l(l+1) \right] \Theta(\theta) = 0. \quad (5.31)$$

We refer to the mathematics lectures for the details about the solution of this equation and give here only a summary of the results. The solutions for $m = 0$ are the Legendre polynomials $\Theta(\theta) = P_l(\cos \theta)$, given by

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l, \quad (5.32)$$

which for the lowest values of l have the form,

$$P_0(x) = 1, \quad P_1(x) = x, \quad P_2(x) = \frac{1}{2}(3x^2 - 1), \quad P_3(x) = \frac{1}{2}(5x^3 - 3x), \dots \quad (5.33)$$

Note that these functions form a set of orthogonal polynomials in x with $-1 \leq x \leq +1$, so that

$$\int_{-1}^{+1} dx P_l(x) P_{l'}(x) = \frac{2\delta_{ll'}}{2l+1}. \quad (5.34)$$

The associated Legendre polynomials, i.e. the solutions of (5.31) for $m > 0$, are

$$P_{l,m}(x) = (1 - x^2)^{m/2} \frac{d^m}{dx^m} P_l(x). \quad (5.35)$$

Alltogether, this results in the orthonormal wave functions,

$$\langle \theta, \phi | l, m \rangle = Y_{l,m}(\theta, \phi) = (-1)^{(m+|m|)/2} e^{im\phi} P_{l,|m|}(\cos \theta) \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}}, \quad (5.36)$$

the so-called *spherical harmonics*. They form an orthonormal basis for wave functions on the unit sphere:

$$\int_{S^2} d\Omega Y_{l,m}^*(\theta, \phi) Y_{l',m'}(\theta, \phi) = \delta_{ll'} \delta_{mm'}, \quad (5.37)$$

where $d\Omega = \sin \theta d\theta d\phi$ and the integration runs over the intervals $0 \leq \phi < 2\pi$ and $0 \leq \theta \leq \pi$. Furthermore, the spherical harmonics have the following properties:

$$Y_{l,-m}(\theta, \phi) = (-1)^m Y_{l,m}^*(\theta, \phi) \quad (5.38)$$

$$Y_{l,m}(\pi - \theta, \phi + \pi) = (-1)^l Y_{l,m}(\theta, \phi), \quad (5.39)$$

where the second equation corresponds to the parity operation $\mathbf{r} \rightarrow -\mathbf{r}$. It follows that the spherical harmonics are also eigenstates of the parity operator with eigenvalue $(-1)^l$. The first spherical harmonics are

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}},$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta, \quad Y_{1,1} = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}, \quad (5.40)$$

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1), \quad Y_{2,1} = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}, \quad Y_{2,2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{i2\phi}.$$

The wave functions with the lowest angular momentum quantum numbers are also called “*s orbital*” for $l = 0$ (*sharp*), “*p orbital*” for $l = 1$ (*principal*), “*d orbital*” for $l = 2$ (*diffuse*), “*f orbital*” for $l = 3$ (*fundamental*), and so on. The *s* orbitals have the highest symmetry, i.e., they are completely rotation invariant.

5.2 Central potentials

We now consider a particle in a potential in three dimensions that is rotationally symmetric centered around $\mathbf{r} = 0$, $V(\mathbf{r}) = V(r)$, where $r = |\mathbf{r}|$. The Hamilton operator has the form

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\hat{r}), \quad (5.41)$$

so that the time-independent Schrödinger equation is

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(\mathbf{r}) = E \psi(\mathbf{r}). \quad (5.42)$$

It is wise to proceed with spherical coordinates: with the representation of the Laplace operator,

$$-\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) - \frac{\hbar^2}{2mr^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right], \quad (5.43)$$

we note that the square bracket can be expressed using $\hat{\mathbf{L}}^2$ from equation (5.27). The Schrödinger equation becomes thus

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{\mathbf{L}}^2}{2mr^2} + V(r)\right]\psi(r, \theta, \phi) = E\psi(r, \theta, \phi). \quad (5.44)$$

We can interpret the first term as the radial contribution to the kinetic energy,

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) = \frac{\hat{p}_r^2}{2m}, \quad (5.45)$$

with the radial momentum operator,

$$\hat{p}_r = \frac{\hbar}{i}\frac{1}{r}\frac{\partial}{\partial r}r, \quad (5.46)$$

so that the commutation relation $[\hat{r}, \hat{p}_r] = i\hbar$ is satisfied. Therefore the Hamilton operator can be written in the form

$$\hat{H} = \frac{\hat{p}_r^2}{2m} + \frac{\hat{\mathbf{L}}^2}{2mr^2} + V(\hat{r}), \quad (5.47)$$

as in classical mechanics.

In this Hamilton operator only $\hat{\mathbf{L}}^2$ and no other term depend on the angle coordinates. It follows that $[\hat{\mathbf{L}}^2, \hat{H}] = 0$ and $[\hat{L}_z, \hat{H}] = 0$. Therefore the eigenstates of \hat{H} can also be chosen to be eigenstates of $\hat{\mathbf{L}}^2$ and \hat{L}_z . Furthermore it holds that with $|\psi\rangle$ also $\hat{L}_{\pm}|\psi\rangle$ is an eigenstate of \hat{H} , and with the same energy eigenvalue, since

$$\hat{H}\hat{L}_{\pm}|\psi\rangle = \hat{L}_{\pm}\hat{H}|\psi\rangle = E\hat{L}_{\pm}|\psi\rangle, \quad (5.48)$$

because of the commutation relations. So if $|\alpha, l, m\rangle$ is an eigenstate of \hat{H} , then all states with $m = -l, -l+1, \dots, l-1, l$ belong to the same energy, which then has the degeneracy $2l+1$. Depending on the exact form of the potential $V(r)$, even higher, but never lower degeneracies can occur.

As a result of this discussion, the eigenfunctions of the Schrödinger equation with a central potential (5.44) are also eigenfunctions of $\hat{\mathbf{L}}^2$ and \hat{L}_z and can be separated into a part depending only on the radial coordinate and a part depending on the angles:

$$\psi_{\alpha,l,m}(r, \theta, \phi) = f_{\alpha,l}(r)Y_{l,m}(\theta, \phi), \quad (5.49)$$

with $Y_{l,m}(\theta, \phi)$ the spherical harmonics and α an energy quantum number.

5.3 Three-dimensional harmonic oscillator

As a first concrete example we examine the harmonic oscillator, which has an exclusively discrete spectrum. In contrast to most of the other non-trivial cases, this problem is already completely solved using the results from the one-dimensional case, since the Hamilton operator can be separated into the different coordinates:

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + \frac{m\omega^2}{2}\hat{\mathbf{r}}^2 = \sum_{\mu=x,y,z} \hat{H}_\mu = \sum_{\mu=x,y,z} \left[\frac{\hat{p}_\mu^2}{2m} + \frac{m\omega^2}{2}\hat{r}_\mu^2 \right]. \quad (5.50)$$

Thus, for each of the three directions we have an independent Hilbert space and each state can be written as a product of three one-dimensional eigenstates (from section 4.1):

$$|n_x, n_y, n_z\rangle = |n_x\rangle \otimes |n_y\rangle \otimes |n_z\rangle \quad \text{with} \quad \hat{H}_\mu |n_\mu\rangle = \hbar\omega \left(n_\mu + \frac{1}{2} \right) |n_\mu\rangle. \quad (5.51)$$

Therefore, the total energy is determined by three quantum numbers,

$$E = \hbar\omega \left(n_x + n_y + n_z + \frac{3}{2} \right), \quad (5.52)$$

where $n_\mu \geq 0$, and is degenerate for $n = n_x + n_y + n_z$.

The ground state is clearly non-degenerate, since there is only one state with $n = 0$. Its wave function is

$$\psi_{0,0,0}(r, \theta, \phi) = \psi_0(x)\psi_0(y)\psi_0(z) = \frac{1}{(r_0\sqrt{\pi})^{3/2}} e^{-\frac{r^2}{2r_0^2}}, \quad (5.53)$$

with $r_0 = \sqrt{\hbar/m\omega}$. On the other hand, we find three degenerate first excited states with $n = 1$, $(n_x, n_y, n_z) = (1, 0, 0), (0, 1, 0), (0, 0, 1)$. The corresponding wave functions are

$$\begin{pmatrix} \psi_{1,0,0}(r, \theta, \phi) \\ \psi_{0,1,0}(r, \theta, \phi) \\ \psi_{0,0,1}(r, \theta, \phi) \end{pmatrix} = \frac{\sqrt{2}}{(r_0\sqrt{\pi})^{3/2}} \begin{pmatrix} x/r_0 \\ y/r_0 \\ z/r_0 \end{pmatrix} e^{-\frac{r^2}{2r_0^2}}, \quad (5.54)$$

which can be written as linear combinations of the spherical harmonics with $l = 1$:

$$\begin{pmatrix} \psi_{1,0,0}(r, \theta, \phi) \\ \psi_{0,1,0}(r, \theta, \phi) \\ \psi_{0,0,1}(r, \theta, \phi) \end{pmatrix} = \sqrt{\frac{2\pi}{3}} \frac{\sqrt{2}re^{-\frac{r^2}{2r_0^2}}}{r_0(r_0\sqrt{\pi})^{3/2}} \begin{pmatrix} -Y_{1,1}(\theta, \phi) + Y_{1,-1}(\theta, \phi) \\ i(Y_{1,1}(\theta, \phi) + Y_{1,-1}(\theta, \phi)) \\ \sqrt{2}Y_{1,0}(\theta, \phi) \end{pmatrix}. \quad (5.55)$$

In other words, the wave functions (5.54) are eigenstates of $\hat{\mathbf{L}}^2$ and not of \hat{L}_z , but we can find a basis of simultaneous eigenstates in the degenerate eigenspace with $n = 1$, in agreement with (5.49).

With growing energy, the degeneracy N_n increases,

$$N_0 = 1, \quad N_1 = 3, \quad N_2 = 6 = 1 + 5, \quad N_3 = 10 = 7 + 3, \quad N_4 = 15 = 1 + 5 + 9, \dots \quad (5.56)$$

We can notice the rule:

$$N_n = \begin{cases} \sum_{l=0,2,4,\dots}^n (2l+1), & n \text{ even} \\ \sum_{l=1,3,5,\dots}^n (2l+1), & n \text{ odd} \end{cases}. \quad (5.57)$$

This behavior can be explained immediately with the help of the angular momentum. The eigenspace with quantum number n apparently contains all angular momentum states corresponding to l from 0 to n (included), where all l are even (odd) if n is even (odd). This behavior is related to parity: the parity of a one-dimensional eigenstate with quantum number n_μ is $(-1)^{n_\mu}$ and thus n fixes the parity of the three-dimensional states by $(-1)^{n_x+n_y+n_z} = (-1)^n$. The parity of $Y_{l,m}$ is equal to $(-1)^l$ and consequently for even n only even l can occur (and vice versa). Remarkably, the degeneracy is larger than only $2l+1$ of a single angular momentum quantum number: this large degeneracy is related with the special form of the potential.

5.4 Bound states in finite potentials

We now return to the general central potential problem, focusing on potentials with $V(r) \leq 0$ and $V(r) \rightarrow 0$ für $r \rightarrow \infty$. Bound states have negative energy, i.e., $r \rightarrow \infty$ corresponds to a classically forbidden zone. We can assign to each state the angular momentum quantum numbers l and m , so that in the position space representation the Schrödinger equation has the form:

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right] \psi(r, \theta, \phi) = E\psi(r, \theta, \phi), \quad (5.58)$$

where we take the Ansatz

$$\psi(r, \theta, \phi) = f(r)Y_{l,m}(\theta, \phi). \quad (5.59)$$

If we write the radial part in the form $f(r) = u(r)/r$, we can simplify the radial derivatives:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right] u(r) = Eu(r). \quad (5.60)$$

This has the form of the one-dimensional Schrödinger equation with the effective potential

$$U(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \quad (5.61)$$

Obviously, the angular momentum introduces a repulsive centrifugal potential ($\propto r^{-2}$).

The function $u(r)$ has to satisfy the conditions

$$u(0) = 0, \quad (5.62)$$

$$u(r) \leq \frac{C}{\sqrt{r}}, \quad \text{für } r \rightarrow \infty, \quad (5.63)$$

where the first one ensures that f does not diverge at $r = 0$, while the second one gives the normalizability of f . The first condition is satisfied if the potential at $r = 0$ is not a δ function. Since, if $u(0) = A \neq 0$, then $\nabla^2 u(0)/r = -4\pi A \delta^{(3)}(\mathbf{r})$ follows, which would lead to a non-solvable situation in (5.58). We now consider the properties in the limits $r \rightarrow 0$ and $r \rightarrow \infty$ for non-diverging potentials.

Limit $r \rightarrow 0$: The centrifugal potential dominates and the Schrödinger equation gives

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} \right] u(r) = 0, \quad (5.64)$$

with the solution $u(r) = ar^{l+1} + br^{-l}$, where $b = 0$ because of $u(0) = 0$. Therefore:

$$f(r \rightarrow 0) \propto r^l. \quad (5.65)$$

Limit $r \rightarrow \infty$: The whole effective potential can be neglected, so that

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} u(r) = Eu(r). \quad (5.66)$$

Thus $u(r) = ce^{-\kappa r}$ with $\kappa = \sqrt{-2mE}/\hbar$, i.e., an exponential decrease of the wave function, in accordance with (5.63). It follows:

$$f(r \rightarrow \infty) \propto \frac{e^{-\kappa r}}{r}. \quad (5.67)$$

Since κ represents an inverse length, we can introduce the dimensionless radial coordinate $\rho = \kappa r$ and the Schrödinger equation (5.60) for u becomes:

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} - \frac{V(\rho/\kappa)}{|E|} - 1 \right] u(\rho) = 0. \quad (5.68)$$

We will use this differential equation for the determination of the energy eigenvalues and eigenstates of the hydrogen atom (in section 5.7).

5.5 Spherical potential well

As an example we consider bound states ($E < 0$) in the spherical potential well

$$V(r) = \begin{cases} -V_0 & r \leq a \\ 0 & r > a \end{cases}, \quad (5.69)$$

with $V_0 > 0$. The Schrödinger equation (5.58) for the radial part of the wave function can be written in the form

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} + 1 \right] f(\rho) = 0, \quad (5.70)$$

where

$$\text{for } r \leq a : \quad \rho = kr \quad \text{with} \quad k = \frac{\sqrt{2m(E + V_0)}}{\hbar}, \quad (5.71)$$

$$\text{for } r > a : \quad \rho = i\kappa r \quad \text{with} \quad \kappa = \frac{\sqrt{-2mE}}{\hbar}, \quad (5.72)$$

take into account the piecewise constant potential.

This differential equation is linear and of second order: for fixed l the spherical Bessel and Neumann functions $j_l(\rho)$ and $n_l(\rho)$ are a basis of the solution space. Alternatively, their linear combinations, the spherical Hankel functions $h_l^{(1)}(\rho) = j_l(\rho) + in_l(\rho)$ and $h_l^{(2)}(\rho) = j_l(\rho) - in_l(\rho)$ are also a basis. The boundary conditions determine which basis choice is more appropriate¹.

For $\rho \rightarrow 0$ we find $j_l(\rho) \propto \rho^l$ and $n_l(\rho) \propto \rho^{-l-1}$. For $\rho \rightarrow \infty$

$$h_l^{(1)}(\rho) \approx -\frac{i}{\rho} e^{i(\rho - l\frac{\pi}{2})} \quad (5.73)$$

holds. This results in the natural Ansatz for $f(r)$:

$$f(r) = \begin{cases} A j_l(kr), & \text{für } r \leq a \\ B h_l^{(1)}(i\kappa r), & \text{für } r > a \end{cases}, \quad (5.74)$$

since in the region $r \leq a$ the at $r = 0$ diverging solution $n_l(kr)$ is not allowed (cf. with (5.65)) and for $r \rightarrow \infty$,

$$h_l^{(1)}(i\kappa r) \approx -\frac{1}{\kappa r} e^{-\kappa r - il\frac{\pi}{2}} \quad (5.75)$$

gives the correct exponential decay (5.67).

The continuity conditions at $r = a$ are:

$$A j_l(ka) = B h_l^{(1)}(i\kappa a), \quad (5.76)$$

$$Ak j'_l(ka) = Bi\kappa h_l^{(1)'}(i\kappa a), \quad (5.77)$$

which we can write as a logarithmic derivative ($f'/f = (\ln f)'$),

$$k \frac{d \ln j_l}{d\rho} \Big|_{\rho=ka} = i\kappa \frac{d \ln h_l^{(1)}}{d\rho} \Big|_{\rho=i\kappa a}, \quad (5.78)$$

in order to eliminate A and B .

The ground state in the potential well will have $l = 0$, because in this case there is no centrifugal barrier: the particle can thus fully benefit from the depth of the potential near $r = 0$ and minimize the energy. For $l = 0$ we have

$$j_0(\rho) = \frac{\sin \rho}{\rho}, \quad (5.79)$$

$$h_0^{(1)} = \frac{\sin \rho}{\rho} - i \frac{\cos \rho}{\rho} = -i \frac{e^{i\rho}}{\rho}, \quad (5.80)$$

¹Appendix B gives a summary of the properties of these functions.

and the condition (5.78) gives

$$\cot ka = -\frac{\kappa}{k} = -\frac{\sqrt{\chi^2 - (ka)^2}}{ka} \quad (5.81)$$

with $\chi = a\sqrt{2mV_0/\hbar}$. This equation has only solutions, if $V_0 > \pi^2\hbar^2/8ma^2$. Therefore, there are bound states in the three-dimensional well only for sufficiently deep and wide potentials. This is completely equivalent to the solutions of odd parity in section 4.4. The unbound states (with $E > 0$) are studied in Quantum Mechanics II, in connection with scattering theory.

5.6 Free particles

In this context it is also possible to study free particles ($V = 0$). The scaled radial Schrödinger equation for $E > 0$ is then again

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} + 1 \right] f(\rho) = 0, \quad (5.82)$$

where

$$\rho = kr \quad \text{with} \quad k = \frac{\sqrt{2m_p E}}{\hbar} \quad (5.83)$$

and m_p is the mass of the particle. Thus the spherical Bessel functions $j_l(kr)$ are now the solutions for all values of $k \in \mathbb{R}$ (the spherical Neumann functions $n_l(kr)$ are not allowed because divergent at $r \rightarrow 0$). Thus, there is a continuous energy spectrum $E = \hbar^2 k^2 / 2m_p$. We can write the wave function in spherical coordinates:

$$\psi_{k,l,m}(r, \theta, \phi) = j_l(kr) Y_{l,m}(\theta, \phi). \quad (5.84)$$

Note that although

$$\lim_{\rho \rightarrow \infty} j_l(\rho) \approx \lim_{\rho \rightarrow \infty} \frac{1}{\rho} \sin \left(\rho - \frac{\pi l}{2} \right) = 0, \quad (5.85)$$

the wave function in \mathbb{R}^3 is not normalizable (exactly as the plane wave), since

$$\int d^3r |\psi_{k,l,m}|^2 \propto \int dr r^2 \left| \frac{\sin(kr)}{kr} \right|^2 \quad (5.86)$$

is divergent.

Therefore, to describe a free particle we can either use a plane wave $\psi_p(r) = e^{ip \cdot r / \hbar}$, with fixed momentum p and energy $E = p^2/2m_p$, or use the wave function $\psi_{k,l,m}$ in (5.84), with fixed angular momentum quantum numbers l , m and energy $E = \hbar^2 k^2 / 2m_p$. However, since, for example, $[\hat{p}_x, \hat{L}_z] \neq 0$ we cannot use both at the same time.

However, it is possible to transform from one representation to the other. One can show, for example, for $\mathbf{p} = \hbar\mathbf{k}$:

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l Y_{l,m}^*(\theta_k, \phi_k) j_l(kr) Y_{l,m}(\theta, \phi), \quad (5.87)$$

where θ_k, ϕ_k (resp. θ, ϕ) are the angles of \mathbf{k} (resp. \mathbf{r}) and $k = |\mathbf{k}|$, $r = |\mathbf{r}|$. Thus we see that a plane wave contains contributions from all eigenstates of $\hat{\mathbf{L}}^2$ and \hat{L}_z . In the special case $\mathbf{k} = k\mathbf{e}_z$, we find

$$e^{ikz} = e^{ikr \cos \theta} = \sum_{l=0}^{\infty} (2l+1) i^l j_l(kr) P_l(\cos \theta), \quad (5.88)$$

with the Legendre polynomials P_l .

5.7 The hydrogen atom

We will now consider the bound states ($E < 0$) for hydrogen-like atoms. The nucleus of such atoms has charge $Q = Ze$ and mass M (for a hydrogen atom $Z = 1$). An electron of charge $-e$ and mass m_e orbits around the nucleus. The Hamilton operator for this two-particle problem is of the form:

$$\hat{H} = \frac{\hat{\mathbf{p}}_1^2}{2M} + \frac{\hat{\mathbf{p}}_2^2}{2m_e} + V(\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2), \quad (5.89)$$

where

$$V(\hat{\mathbf{r}}) = -\frac{Ze^2}{|\hat{\mathbf{r}}|} \quad (5.90)$$

is the Coulomb potential and $\hat{\mathbf{r}}_1, \hat{\mathbf{p}}_1$ (resp. $\hat{\mathbf{r}}_2, \hat{\mathbf{p}}_2$) are the position and momentum operators for the nucleus (resp. the electron).

We introduce the center-of-mass and relative coordinates:

$$\hat{\mathbf{p}}_S = \hat{\mathbf{p}}_1 + \hat{\mathbf{p}}_2 \quad \text{and} \quad \hat{\mathbf{r}}_S = \frac{M\hat{\mathbf{r}}_1 + m_e\hat{\mathbf{r}}_2}{M + m_e} \quad (5.91)$$

$$\hat{\mathbf{p}}_R = \frac{m_e\hat{\mathbf{p}}_1 - M\hat{\mathbf{p}}_2}{M + m_e} \quad \text{and} \quad \hat{\mathbf{r}}_R = \hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2, \quad (5.92)$$

from which we get a separation of the center-of-mass and relative motions,

$$\frac{\hat{\mathbf{p}}_1^2}{2M} + \frac{\hat{\mathbf{p}}_2^2}{2m_e} = \frac{\hat{\mathbf{p}}_S^2}{2M_S} + \frac{\hat{\mathbf{p}}_R^2}{2\mu}, \quad (5.93)$$

with the total mass $M_S = M + m_e$ and the reduced mass $\mu = Mm_e/M_S$. Since the Hamilton operators of the center-of-mass motion ($\hat{H}_S = \hat{\mathbf{p}}_S^2/2M_S$) and of the relative motion ($\hat{H}_R = \hat{\mathbf{p}}_R^2/2\mu + V(\hat{\mathbf{r}}_R)$) commutes (since $[\hat{p}_{S,i}, \hat{r}_{R,j}] = 0$), we can treat the two dynamics separately. The potential depends only on the relative coordinate $\hat{\mathbf{r}}_R$.

The center-of-mass motion is therefore that of a free particle. The relative motion corresponds to the motion of a particle with mass μ in the Coulomb potential, which is what we will focus on now.

In spherical coordinates, the time-independent Schrödinger equation of the relative motion is

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{r} \right] \psi(r, \theta, \phi) = E\psi(r, \theta, \phi). \quad (5.94)$$

With the definitions of section 5.4, $\psi(r, \theta, \phi) = \frac{u(r)}{r} Y_{l,m}(\theta, \phi)$, we can rescale the radial coordinate, $r = \kappa\rho$ with $\kappa = \sqrt{-2\mu E}/\hbar$, and find the Schrödinger equation (5.68) for the radial function u :

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{\rho_0}{\rho} - 1 \right] u(\rho) = 0, \quad (5.95)$$

where

$$\rho_0 = -\frac{Ze^2\kappa}{E} = \frac{Ze^2}{\hbar} \sqrt{\frac{2\mu}{-E}}. \quad (5.96)$$

(Notice that we are looking for bound states and therefore $E < 0$.)

We use the known asymptotic behavior of u for $\rho \rightarrow 0$ and ∞ to write the Ansatz

$$u(\rho) = \rho^{l+1} e^{-\rho} w(\rho). \quad (5.97)$$

This leads to the differential equation for w :

$$\rho \frac{d^2 w}{d\rho^2} + 2(l+1-\rho) \frac{dw}{d\rho} + (\rho_0 - 2(l+1))w = 0, \quad (5.98)$$

which we solve using a power series (Sommerfeld method):

$$w(\rho) = \sum_{k=0}^{\infty} a_k \rho^k. \quad (5.99)$$

Inserting the series in (5.98) and performing a comparison of the coefficients we find the recursion identity:

$$a_{k+1} = \frac{2(k+l+1) - \rho_0}{(k+1)(k+2l+2)} a_k. \quad (5.100)$$

If the series is infinite, $a_{k+1}/a_k \rightarrow 2/k$ für $k \rightarrow \infty$. Thus $a_k \approx 2^k a_0/k!$ and $w(\rho)$ would grow like $e^{2\rho}$. Consequently $u(\rho)$ would diverge for $\rho \rightarrow \infty$, which would not lead to a normalizable wave function. Consequently, the power series cannot be infinite, but must stop at finite k . This occurs if the factor in the recursion formula (5.100) vanishes for some $k = N$, i.e., we arrive at the condition that

$$2(N+l+1) = \rho_0 = \frac{Ze^2}{\hbar} \sqrt{-\frac{2\mu}{E}} \quad \text{with } N = 0, 1, 2, 3, \dots \quad (5.101)$$

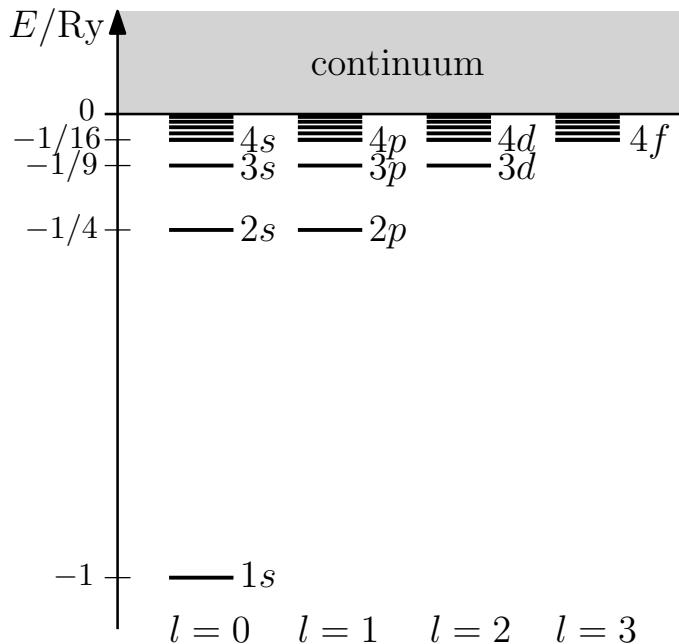


Figure 5.2: Energy spectrum of the hydrogen atom.

By solving, we obtain the Bohr-Sommerfeld spectrum,

$$E = -\frac{Z^2 e^4 \mu}{2\hbar^2 (N+l+1)^2} = -\frac{Z^2 e^4 \mu}{2\hbar^2 n^2} = E_n, \quad (5.102)$$

with $n = N + l + 1$ as principal quantum number. The energy eigenvalue E_n depends only on $n = N + l + 1$. With this we can calculate the possible angular momentum states and the degeneracy of the states with energy E_n can be easily determined. For a given n , N can be equal to $0, 1, 2, \dots, n-1$, and we find the possible angular momentum quantum numbers $l = 0, 1, 2, \dots, n-1$. Each angular momentum quantum number brings the degeneracy $2l+1$, since the energy does not depend on $m = -l, \dots, +l$. Thus, the total number of degenerate states amounts to

$$\sum_{l=0}^{n-1} (2l+1) = n^2. \quad (5.103)$$

This extraordinarily high degeneracy (even higher than that of the harmonic oscillator) is a special property of the Coulomb potential and is related to the existence of a further conserved quantity: the Laplace-Runge-Lenz-Pauli vector,

$$\widehat{\mathbf{W}} = \frac{1}{2\mu} [\widehat{\mathbf{p}}_R \times \widehat{\mathbf{L}}_R - \widehat{\mathbf{L}}_R \times \widehat{\mathbf{p}}_R] - \frac{Ze^2}{|\widehat{\mathbf{r}}_R|} \widehat{\mathbf{r}}_R. \quad (5.104)$$

One can show that this operator commutes with the Hamilton operator and is responsible for the n^2 degeneracy of the energy eigenvalues².

²See Gordon Baym, *Lectures on Quantum Mechanics*, Addison-Wesley.

We now consider some characteristic quantities. The exponential decay of the radial function, given by $e^{-\kappa r}$, defines a length scale:

$$\kappa^{-1} = \frac{\hbar}{\sqrt{-2\mu E_n}} = \frac{\hbar^2 n}{Ze^2 \mu} = \frac{na_0}{Z} = \kappa_n^{-1}, \quad (5.105)$$

where a_0 is the Bohr radius defined in the first chapter:

$$a_0 = \frac{\hbar^2}{\mu e^2} \approx 0.529 \times 10^{-10} \text{m} \quad (5.106)$$

(with the reduced mass $\mu \approx m_e$). The energy levels (in fig. 5.2) are

$$E_n = -\frac{Z^2 e^2}{2a_0 n^2} = -\frac{\mu c^2}{2} \alpha^2 \frac{Z^2}{n^2}, \quad (5.107)$$

with $\alpha = e^2/\hbar c = 1/137$ the fine structure constant. The ionization energy, corresponding to the binding energy of the ground state ($n = 1$), is

$$E_I = Z^2 13.6 \text{eV} = Z^2 \text{Ry}, \quad (5.108)$$

which defines the energy unit *Rydberg*. Note that the energy of the hydrogen atom is bounded from below and the atom is therefore stable! This is in contrast to the classical hydrogen atom, where the (accelerated) electron would lose arbitrarily much energy through radiation (see electrodynamics).

The functions $w(\rho)$ correspond to the so-called Laguerre polynomials,

$$w(\rho) = A_{n,l} L_{n+l}^{2l+1}(2\rho), \quad (5.109)$$

with $A_{n,l}$ a normalization constant and

$$L_r^s(x) = \frac{(-1)^s}{r!} \frac{d^s}{dx^s} e^x \frac{d^r}{dx^r} e^{-x} x^r. \quad (5.110)$$

The total wave function is

$$\psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi), \quad (5.111)$$

with the radial wave function $R_{n,l}$, which has the form (for the lowest energy eigen-

states):

$$\begin{aligned}
 R_{1,0}(r) &= 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-\frac{Zr}{a_0}}, && \text{K shell, s orbital,} \\
 R_{2,0}(r) &= 2 \left(\frac{Z}{2a_0} \right)^{3/2} \left(1 - \frac{Zr}{2a_0} \right) e^{-\frac{Zr}{2a_0}}, && \text{L shell, s orbital,} \\
 R_{2,1}(r) &= \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}}, && \text{L shell, p orbital,} \\
 R_{3,0}(r) &= 2 \left(\frac{Z}{3a_0} \right)^{3/2} \left(1 - \frac{2Zr}{3a_0} + \frac{2Z^2r^2}{27a_0^2} \right) e^{-\frac{Zr}{3a_0}}, && \text{M shell, s orbital,} \\
 R_{3,1}(r) &= \frac{4\sqrt{2}}{9} \left(\frac{Z}{3a_0} \right)^{3/2} \frac{Zr}{a_0} \left(1 - \frac{Zr}{6a_0} \right) e^{-\frac{Zr}{3a_0}}, && \text{M shell, p orbital,} \\
 R_{3,2}(r) &= \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Z}{3a_0} \right)^{3/2} \left(\frac{Zr}{a_0} \right)^2 e^{-\frac{Zr}{3a_0}}, && \text{M shell, d orbital.}
 \end{aligned} \tag{5.112}$$

The experimentally observable spectra originate from transitions between states of different energy levels. Certain selection rules apply, which are determined by the symmetry of the states and by the form of stimulation of the transition. For optical transitions, the angular momentum quantum number l is changed by 1. We give here a list of the most known spectra:

Series	n_{End}	wavelength range
Lyman	1	ultraviolet ca. 100 nm
Balmer	2	ultraviolet-visible (400-600 nm)
Paschen	3	infrared (1000 - 7000 nm)
Brackett	4	infrared (1000 - 7000 nm)
Pfund	5	infrared (1000 - 7000 nm)

5.8 Atoms in a magnetic field

We have seen that the energy eigenstates of the hydrogen atom are highly degenerate. However, one can partially split this degeneracy by, for example, placing the atom in an external magnetic field. This is what we want to investigate here ³.

³We consider here only the effects of the orbital angular momentum $\hat{\mathbf{L}}$ and neglect electron spin. The full discussion will come in chapter 9.

We first consider in general a particle with charge q and mass m subject to an electromagnetic field:

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} - \nabla \Phi, \quad \mathbf{B} = \nabla \times \mathbf{A}, \quad (5.113)$$

with the potentials \mathbf{A} and Φ . We still have a freedom to choose these potentials, since the gauge transformation

$$\mathbf{A} \rightarrow \mathbf{A} + \nabla \chi \quad \text{and} \quad \Phi \rightarrow \Phi - \frac{1}{c} \frac{\partial \chi}{\partial t} \quad (5.114)$$

leaves all measurable quantities invariant. As seen in section 2.3, the Hamilton operator has the form

$$\hat{H} = \frac{1}{2m} \left(\hat{\mathbf{p}} - \frac{q}{c} \mathbf{A}(\hat{\mathbf{r}}) \right)^2 + q\Phi(\hat{\mathbf{r}}). \quad (5.115)$$

We consider a uniform magnetic field along the z axis, $\mathbf{B} = (0, 0, B)$. With the choice of the Coulomb gauge, $\nabla \cdot \mathbf{A} = 0$, we introduce the vector potential as

$$\mathbf{A}(\hat{\mathbf{r}}) = -\frac{1}{2}(\hat{\mathbf{r}} \times \mathbf{B}). \quad (5.116)$$

With this choice we have $\hat{\mathbf{p}} \cdot \mathbf{A}(\hat{\mathbf{r}}) = \mathbf{A}(\hat{\mathbf{r}}) \cdot \hat{\mathbf{p}}$, and therefore

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + q\Phi(\hat{\mathbf{r}}) + \frac{q}{2mc}(\hat{\mathbf{r}} \times \mathbf{B}) \cdot \hat{\mathbf{p}} + \frac{q^2}{8mc^2}(\hat{\mathbf{r}} \times \mathbf{B})^2. \quad (5.117)$$

With $(\hat{\mathbf{r}} \times \mathbf{B})^2 = B^2(\hat{x}^2 + \hat{y}^2)$ and $(\hat{\mathbf{r}} \times \mathbf{B}) \cdot \hat{\mathbf{p}} = -(\hat{\mathbf{r}} \times \hat{\mathbf{p}}) \cdot \mathbf{B} = -\hat{\mathbf{L}} \cdot \mathbf{B} = -\hat{L}_z B$ we find:

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + q\Phi(\hat{\mathbf{r}}) - \frac{q}{2mc}\hat{L}_z B + \frac{q^2}{8mc^2}B^2(\hat{x}^2 + \hat{y}^2). \quad (5.118)$$

For an electron in a hydrogen atom, $q = -e$ and Φ is the Coulomb potential of the nucleus. Thus $\hat{H}_0 = \hat{\mathbf{p}}^2/2m_e + q\Phi(\hat{\mathbf{r}})$ is the Hamilton operator of the unperturbed atom. The last two terms cause a shift in the energy for an isolated atom: we would like to estimate their contribution in a small magnetic field:

$$\frac{\frac{e^2}{8mc^2}B^2\langle\hat{x}^2 + \hat{y}^2\rangle}{\frac{e}{2m_e}B\langle L_z\rangle} \approx \frac{eB}{4c} \frac{a_0^2}{\hbar} \approx 10^{-10}B \quad (\text{in Gauss}), \quad (5.119)$$

where we used the approximations $\langle\hat{x}^2 + \hat{y}^2\rangle \approx a_0^2$ (a_0 the Bohr radius) and $\langle L_z \rangle \approx \hbar$. For magnetic fields achievable in the laboratory, the effect of the term with \hat{L}_z for an atom is much larger than the term with $\hat{x}^2 + \hat{y}^2$. The first term is the paramagnetic and the second the diamagnetic contribution to the Hamilton operator. However, the diamagnetic contribution becomes comparable as soon as the electron orbitals are extended in space, as in metals where the electrons are essentially free to move.

Neglecting the diamagnetic term, we can write the Hamilton operator as

$$\hat{H} = \hat{H}_0 + \frac{e}{2m_e c} B \hat{L}_z. \quad (5.120)$$

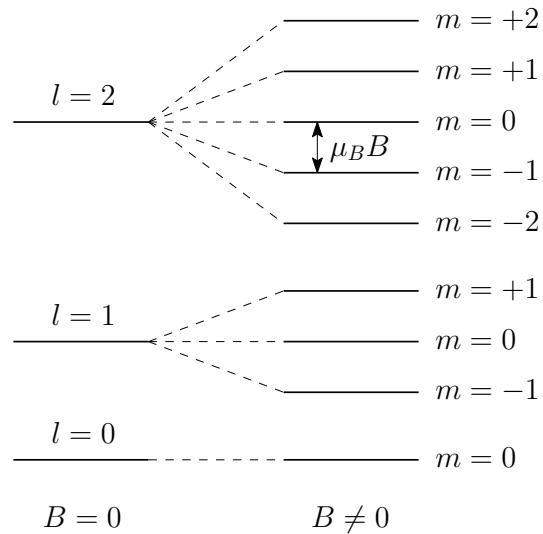


Figure 5.3: Splitting of the energy levels in a magnetic field.

\hat{L}_z commutes with the unperturbed Hamilton operator \hat{H}_0 , because of the spherically symmetric potential, and we can thus find common eigenstates. These are, of course, the eigenstates that we found for the hydrogen atom in the previous section. The hydrogen states $|n, l, m\rangle$ give energies

$$E_{n,l,m} = -\frac{1\text{Ry}}{n^2} + \frac{e}{2m_e c} \hbar m B = -\frac{1\text{Ry}}{n^2} + \hbar \omega_L m = -\frac{1\text{Ry}}{n^2} + m \mu_B B, \quad (5.121)$$

where $\omega_L = eB/2m_e c$ is the Larmor frequency and $\mu_B = e\hbar/2m_e c = 0.93 \times 10^{-20}\text{erg/G}$ the Bohr magneton. It turns out that the magnetic field partially splits the degeneracy of the states: the so-called Zeeman effect (Fig. 5.3).

The splitting of the energy levels is very small compared to the original spacing of the low energy levels, for experimentally achievable fields ($B < 2 \times 10^6\text{G} = 20\text{T}$):

$$\frac{e\hbar B}{2m_e c} \approx 4\text{Ry} \times 10^{-10} B \quad (\text{in Gauss}). \quad (5.122)$$

The energy change of the atomic levels in the magnetic field means that the states have a magnetic moment, which is defined as

$$\underbrace{\text{magnetic moment}}_{\mathbf{M}_p} = -\frac{\partial E}{\partial \mathbf{B}} = -\frac{e}{2m_e c} \mathbf{L} = -\frac{\mu_B}{\hbar} \mathbf{L}. \quad (5.123)$$

The atomic magnetic moment induced by the angular momentum is approximately

$$|\langle \mathbf{M}_p \rangle| = \frac{\mu_B}{\hbar} |\langle \mathbf{L} \rangle| \approx \mu_B. \quad (5.124)$$

The diamagnetic moment

$$\langle \mathbf{M}_d \rangle = -\frac{e^2}{4m_e c^2} \langle \hat{x}^2 + \hat{y}^2 \rangle \mathbf{B} \approx -\frac{e^2 a_0^2}{4m_e c^2} \mathbf{B} \quad (5.125)$$

is comparatively small.

Chapter 6

Symmetries and conserved quantities

As we have already seen in some examples (e.g. periodic, rotationally invariant or mirror symmetric potentials), continuous and discrete symmetries allow us to characterize states of a quantum mechanical system and to determine conservation laws, which often appear as quantum numbers of the system. There is therefore a close relation between the symmetries and the quantum numbers of a quantum mechanical system: we would like to look at this relation in more detail.

6.1 Continuous unitary transformations

A system is symmetric if it is invariant under the action of a symmetry group \mathcal{G} . For a quantum mechanical system, we require that the symmetry transformations are compatible with the structures of quantum mechanics, namely with the vector space structure and with the scalar product defined there. The simplest way to achieve this aim is realized by letting the group \mathcal{G} act on the Hilbert space \mathcal{H} by means of unitary operators. The linearity of the operators respects the vector space structure, their unitarity leaves the scalar product invariant.

We consider first continuous transformations, i.e. transformations which depend on a continuous parameter, like translations and rotations. A general continuous unitary transformation operator can be written as

$$\hat{U}(s) = e^{\pm \frac{i}{\hbar} s \hat{K}}, \quad (6.1)$$

where \hat{K} is a Hermitian operator and s a real parameter, which denotes a group element $g \in \mathcal{G}$. We will see that for example s can be a translation length or a rotation angle. The operator \hat{K} is called *generator* of the unitary transformations $\hat{U}(s)$.

We have already encountered such a unitary transformation operator: the time evolution operator $e^{-i\hat{H}t/\hbar}$ for a time-independent Hamilton operator \hat{H} . In this context, it can be interpreted as a transformation operator for translations in time: $e^{-i\hat{H}t/\hbar}|\psi(t_0)\rangle = |\psi(t_0 + t)\rangle$. The time evolution operator describes a symmetry of the system because the Hamilton operator does not depend on time and thus $[e^{-i\hat{H}t/\hbar}, \hat{H}] = 0$ for all times t . It follows trivially that $[\hat{H}, \hat{H}] = 0$, i.e., the energy is conserved (what we obviously already knew in this case).

The unitary transformations generated by \hat{K} form a group, i.e., the product of two such transformations is also a transformation: if s_1 (s_2) belongs to the group element g_1 (g_2), then the multiplication results in

$$\hat{U}(s_1)\hat{U}(s_2) = \hat{U}(s_3), \quad (6.2)$$

where the transformation $\hat{U}(s_3)$ corresponds to the group element $g_3 = g_1 * g_2$ (we denote with $*$ the group operation in \mathcal{G}). Moreover, the multiplication is associative, there exists a neutral element, $\hat{1} = \hat{U}(0)$ and for each $\hat{U}(s)$ there is an inverse element $\hat{U}(s)^{-1} = \hat{U}^\dagger(s) = \hat{U}(-s)$ with $\hat{U}(s)\hat{U}(s)^{-1} = \hat{1}$. In mathematics, $\hat{U}(s)$ is called a representation of the group \mathcal{G} .¹

The transformation of a state $|\psi\rangle \in \mathcal{H}$ is given by

$$|\psi'\rangle = \hat{U}(s)|\psi\rangle, \quad (6.3)$$

and thus an operator \hat{A} transforms as

$$\hat{A}' = \hat{U}(s)\hat{A}\hat{U}(s)^\dagger, \quad (6.4)$$

so that $(\hat{A}|\psi\rangle)' = \hat{U}(s)\hat{A}|\psi\rangle = \hat{U}(s)\hat{A}\hat{U}(s)^\dagger\hat{U}(s)|\psi\rangle = \hat{A}'|\psi'\rangle$ holds. We point out here an analogy between these symmetry transformations and the relation between Schrödinger's and Heisenberg's picture for time evolution. The transformation of a quantum mechanical system is implemented (for example for the evaluation of expectation values), by transforming either the states or the operators, not both simultaneously. In fact, the transformations (6.3) and (6.4) are defined in such a way that the simultaneous transformation of states and operators would always leave all expectation values and matrix elements unchanged,

$$\langle\psi'|\hat{A}'|\phi'\rangle = \langle\psi|\hat{U}(s)^\dagger\hat{U}(s)\hat{A}\hat{U}(s)^\dagger\hat{U}(s)|\phi\rangle = \langle\psi|\hat{A}|\phi\rangle, \quad (6.5)$$

for all operators \hat{A} and states $|\psi\rangle$, $|\phi\rangle$.

Assuming that the group \mathcal{G} is a symmetry of the system, i.e., that the Hamilton operator \hat{H} is invariant under the transformation $\hat{U}(s)$ generated by \hat{K} :

$$[\hat{H}, \hat{U}(s)] = 0, \quad \text{for all } s, \quad (6.6)$$

or, equivalently,

$$[\hat{H}, \hat{K}] = 0, \quad (6.7)$$

then for an eigenstate $|\psi\rangle$ with $\hat{H}|\psi\rangle = E|\psi\rangle$ it follows that $|\psi'\rangle = \hat{U}(s)|\psi\rangle$ is also an eigenstate, with the same energy, since

$$\hat{H}\hat{U}(s)|\psi\rangle = \hat{U}(s)\hat{H}|\psi\rangle = E\hat{U}(s)|\psi\rangle. \quad (6.8)$$

Since \hat{K} commutes with the Hamilton operator, both operators have common eigenstates. Thus \hat{K} corresponds to a conserved quantity of the system and its eigenvalues are good quantum numbers. Furthermore, from the equation of motion in the Heisenberg representation follows:

$$\frac{d}{dt}\langle\hat{K}\rangle = \frac{d}{dt}\langle\phi|\hat{K}(t)|\phi\rangle = \frac{i}{\hbar}\langle\phi|[\hat{H}, \hat{K}]|\phi\rangle = 0, \quad (6.9)$$

¹See Appendix C for a summary on groups and their representation theory.

i.e., the expectation value of \hat{K} is a constant of the motion for every state ϕ (not only for eigenstates). We can conclude that for any (continuous) symmetry there exists a conserved quantity. We will now consider two examples: translations and rotations.

6.2 Translation symmetry

The generating operator for translations is the momentum operator $\hat{\mathbf{p}}$. The translation by a vector \mathbf{a} is

$$\hat{U}(\mathbf{a}) = e^{\frac{i}{\hbar} \hat{\mathbf{p}} \cdot \mathbf{a}}. \quad (6.10)$$

For the position operator, using (3.47),

$$\hat{\mathbf{r}}' = \hat{U}(\mathbf{a}) \hat{\mathbf{r}} \hat{U}(\mathbf{a})^\dagger = \hat{\mathbf{r}} + \frac{i}{\hbar} [\mathbf{a} \cdot \hat{\mathbf{p}}, \hat{\mathbf{r}}] = \hat{\mathbf{r}} + \mathbf{a} \quad (6.11)$$

holds, which indeed corresponds to a translation by \mathbf{a} . Applied to a basis state in the position representation, the translation operator yields

$$\hat{U}(\mathbf{a})|\mathbf{r}\rangle = |\mathbf{r} - \mathbf{a}\rangle, \quad (6.12)$$

$$\hat{U}(\mathbf{a})^\dagger|\mathbf{r}\rangle = \hat{U}(-\mathbf{a})|\mathbf{r}\rangle = |\mathbf{r} + \mathbf{a}\rangle, \quad (6.13)$$

$$\langle \mathbf{r} | \hat{U}(\mathbf{a}) = \langle \mathbf{r} + \mathbf{a} |, \quad (6.14)$$

$$\langle \mathbf{r} | \hat{U}(\mathbf{a})^\dagger = \langle \mathbf{r} - \mathbf{a} |, \quad (6.15)$$

since in this way the matrix elements $\langle \mathbf{r}_1 | \hat{U}(\mathbf{a}) \hat{\mathbf{r}} \hat{U}(\mathbf{a})^\dagger | \mathbf{r}_2 \rangle$ are the same:

$$\langle \mathbf{r}_1 | \hat{U}(\mathbf{a}) \hat{\mathbf{r}} \hat{U}(\mathbf{a})^\dagger | \mathbf{r}_2 \rangle = \langle \mathbf{r}_1 | \hat{\mathbf{r}} + \mathbf{a} | \mathbf{r}_2 \rangle = (\mathbf{r}_2 + \mathbf{a}) \delta^{(3)}(\mathbf{r}_1 - \mathbf{r}_2), \quad (6.16)$$

$$\langle \mathbf{r}_1 | \hat{U}(\mathbf{a}) \hat{\mathbf{r}} \hat{U}(\mathbf{a})^\dagger | \mathbf{r}_2 \rangle = \langle \mathbf{r}_1 + \mathbf{a} | \hat{\mathbf{r}} | \mathbf{r}_2 + \mathbf{a} \rangle = (\mathbf{r}_2 + \mathbf{a}) \delta^{(3)}(\mathbf{r}_1 - \mathbf{r}_2). \quad (6.17)$$

Therefore, for the wave function of the state $|\psi'\rangle = \hat{U}(\mathbf{a})|\psi\rangle$ we have:

$$\psi'(\mathbf{r}) = \langle \mathbf{r} | \psi' \rangle = \langle \mathbf{r} | \hat{U}(\mathbf{a}) | \psi \rangle = \langle \mathbf{r} + \mathbf{a} | \psi \rangle = \psi(\mathbf{r} + \mathbf{a}), \quad (6.18)$$

i.e., the wave function undergoes a “passive” translation, by transforming its argument \mathbf{r} .

An important note: we have chosen the convention,² in which the translation operator $\hat{U}(\mathbf{a})$ shifts the operators (and their spectra) by $+\mathbf{a}$. With the condition that the simultaneous transformation of operators and states leaves the expectation values invariant, the states are then shifted by $\hat{U}(\mathbf{a})$ in the opposite direction by $-\mathbf{a}$, which corresponds to the “passive” translation mentioned above. If one wants to shift the state by $+\mathbf{a}$, then one must act on it with $\hat{U}(-\mathbf{a}) = \hat{U}(\mathbf{a})^\dagger$.

One can obtain the same relation by considering the effect of an infinitesimal translation $\delta\mathbf{a}$. From $\langle \mathbf{r} | \hat{\mathbf{p}} | \psi \rangle = -i\hbar \nabla \psi(\mathbf{r})$ follows:

$$\langle \mathbf{r} | \hat{U}(\delta\mathbf{a}) | \psi \rangle = \langle \mathbf{r} | e^{\frac{i}{\hbar} \hat{\mathbf{p}} \cdot \delta\mathbf{a}} | \psi \rangle \approx \langle \mathbf{r} | 1 + \frac{i}{\hbar} \hat{\mathbf{p}} \cdot \delta\mathbf{a} | \psi \rangle = \psi(\mathbf{r}) + \delta\mathbf{a} \cdot \nabla \psi(\mathbf{r}). \quad (6.19)$$

²The opposite choice, $e^{-i\hat{\mathbf{p}} \cdot \mathbf{a}/\hbar}$, is also possible and is found in the literature.

This is exactly the first order term in the Taylor approximation for $\psi(\mathbf{r} + \delta\mathbf{a})$.

Since all components of $\hat{\mathbf{p}}$ commute with each other, we have

$$\hat{U}(\mathbf{a}_1)\hat{U}(\mathbf{a}_2) = \hat{U}(\mathbf{a}_2)\hat{U}(\mathbf{a}_1) = \hat{U}(\mathbf{a}_1 + \mathbf{a}_2) \quad (6.20)$$

i.e., the group of the translations is Abelian. Furthermore, it is clear that the group is infinite, since each translation vector \mathbf{a} corresponds to a group element. The irreducible representations of this group are all one-dimensional and can be represented in momentum space as

$$\langle \mathbf{p}' | \hat{U}(\mathbf{a}) | \mathbf{p} \rangle = e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{a}} \delta^{(3)}(\mathbf{p} - \mathbf{p}') \quad (6.21)$$

i.e., each momentum \mathbf{p} corresponds to a single representation of the group as $e^{i\mathbf{p} \cdot \mathbf{a}/\hbar}$.

For a translation invariant system commutes $\hat{\mathbf{p}}$ with the Hamilton operator. Then the momentum eigenstates are also energy eigenstates and \mathbf{p} is a good quantum number, since the eigenstates are plane waves, $\psi_{\mathbf{p}}(\mathbf{r}) = e^{i\mathbf{p} \cdot \mathbf{r}/\hbar}$. This also means that the wave function with momentum quantum number \mathbf{p} satisfies the following relation:

$$\psi'_{\mathbf{p}}(\mathbf{r}) = \psi_{\mathbf{p}}(\mathbf{r} + \mathbf{a}) = \langle \mathbf{r} + \mathbf{a} | \mathbf{p} \rangle = \langle \mathbf{r} | \hat{U}(\mathbf{a}) | \mathbf{p} \rangle = e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{a}} \langle \mathbf{r} | \mathbf{p} \rangle = e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{a}} \psi_{\mathbf{p}}(\mathbf{r}). \quad (6.22)$$

For the basis wave functions of the one-dimensional irreducible representations, the transformation consists only of a multiplication by a phase factor, which of course leaves the normalization unchanged.

6.3 Rotation symmetry

Let $R \in \text{SO}(3)$ be a rotation of the three-dimensional space³, with rotation axis \mathbf{n} (with $|\mathbf{n}| = 1$) and rotation angle α . Applied to a vector $\mathbf{r} \in \mathbb{R}^3$ it gives the rotated vector $\mathbf{r}' = R\mathbf{r}$. For transformations in the Hilbert space, the angular momentum operator $\hat{\mathbf{L}}$ takes the role of the generating operator: the rotation operator has the form

$$\hat{U}(\alpha) = e^{\frac{i}{\hbar} \alpha \cdot \hat{\mathbf{L}}}, \quad (6.23)$$

where $\alpha = \alpha \mathbf{n}$. This becomes apparent when we consider an infinitesimal rotation $\delta\alpha$. Applied to the position operator $\hat{\mathbf{r}}$ this results in

$$\hat{U}(\delta\alpha)\hat{\mathbf{r}}\hat{U}(\delta\alpha)^{\dagger} = \hat{\mathbf{r}} + \frac{i}{\hbar} [\delta\alpha \cdot \hat{\mathbf{L}}, \hat{\mathbf{r}}] + \mathcal{O}(\delta\alpha^2) = \hat{\mathbf{r}} + \delta\alpha \times \hat{\mathbf{r}} + \dots, \quad (6.24)$$

where we used (3.47) and (5.3). The last expression is exactly the relation we expect for an infinitesimal rotation of coordinates. For general rotations then we find

$$\hat{U}(\alpha)\hat{\mathbf{r}}\hat{U}(\alpha)^{\dagger} = \hat{\mathbf{r}}', \quad (6.25)$$

with $\hat{\mathbf{r}}'$ the operator of the rotated coordinates, $\hat{\mathbf{r}}' = R\hat{\mathbf{r}}$.

³ $\text{SO}(3) = \{R \in \mathbb{R}^{3 \times 3} | R^T R = 1, \det R = 1\}$ is the special orthogonal group.

Applied to a position basis state, the rotation operator (analogously to the translation operator) yields

$$\hat{U}(\boldsymbol{\alpha})|\mathbf{r}\rangle = |R^{-1}\mathbf{r}\rangle, \quad (6.26)$$

$$\hat{U}(\boldsymbol{\alpha})^\dagger|\mathbf{r}\rangle = \hat{U}(-\boldsymbol{\alpha})|\mathbf{r}\rangle = |R\mathbf{r}\rangle, \quad (6.27)$$

$$\langle \mathbf{r}|\hat{U}(\boldsymbol{\alpha}) = \langle R\mathbf{r}|, \quad (6.28)$$

$$\langle \mathbf{r}|\hat{U}(\boldsymbol{\alpha})^\dagger = \langle R^{-1}\mathbf{r}|, \quad (6.29)$$

where R^{-1} is the inverse rotation (with the same axis and angle $-\alpha$). As with translations, rotations act passively on the wave function of a state:

$$\psi'(\mathbf{r}) = \langle \mathbf{r}|\hat{U}(\boldsymbol{\alpha})|\psi\rangle = \langle R\mathbf{r}|\psi\rangle = \psi(R\mathbf{r}) = \psi(\mathbf{r}'). \quad (6.30)$$

Since the three components of the angular momentum do not commute with each other, in general

$$\hat{U}(\boldsymbol{\alpha}_1)\hat{U}(\boldsymbol{\alpha}_2) \neq \hat{U}(\boldsymbol{\alpha}_2)\hat{U}(\boldsymbol{\alpha}_1) \quad (6.31)$$

holds. The group of all rotations is non-Abelian, and consequently there are also higher dimensional irreducible representations. It can be shown that for each odd dimension there is exactly one irreducible representation: the basis states of these irreducible representations are the eigenstates of angular momentum, more precisely those of $\hat{\mathbf{L}}^2$ and \hat{L}_z , i.e. $|l, m\rangle$, with integer quantum number l .⁴ One can think of these representations as follows: $[\hat{\mathbf{L}}, \hat{\mathbf{L}}^2] = 0$ holds and thus also $[\hat{U}(\boldsymbol{\alpha}), \hat{\mathbf{L}}^2] = [e^{\frac{i}{\hbar}\boldsymbol{\alpha}\cdot\hat{\mathbf{L}}}, \hat{\mathbf{L}}^2] = 0$, i.e., under rotations the quantum number l of $\hat{\mathbf{L}}^2$ is preserved,

$$\hat{\mathbf{L}}^2\hat{U}(\boldsymbol{\alpha})|l, m\rangle = \hat{U}(\boldsymbol{\alpha})\hat{\mathbf{L}}^2|l, m\rangle = \hbar^2 l(l+1)\hat{U}(\boldsymbol{\alpha})|l, m\rangle, \quad (6.32)$$

only the quantum number m of \hat{L}_z can change. The rotation operator applied to $|l, m\rangle$ gives a linear combination of the states with the same quantum number l :

$$\hat{U}(\boldsymbol{\alpha})|l, m\rangle = \sum_{m'=-l}^{+l} d_{m',m}^{(l)}(\boldsymbol{\alpha})|l, m'\rangle, \quad (6.33)$$

with the coefficients

$$d_{m',m}^{(l)}(\boldsymbol{\alpha}) = \langle l, m'|e^{\frac{i}{\hbar}\boldsymbol{\alpha}\cdot\hat{\mathbf{L}}}|l, m\rangle. \quad (6.34)$$

These coefficients are the matrix elements of the irreducible representation in the basis $|l, m\rangle$. For every integer l there is such a representation, with odd dimension $2l+1$. The representation with $l=0$ is one-dimensional and corresponds to the trivial representation. The matrices $d^{(l)}(\boldsymbol{\alpha})$ are unitary:

$$(d^{(l)}(\boldsymbol{\alpha})^\dagger)_{m',m} = d_{m,m'}^{(l)}(\boldsymbol{\alpha})^* = \langle l, m'|e^{-\frac{i}{\hbar}\boldsymbol{\alpha}\cdot\hat{\mathbf{L}}}|l, m\rangle = d_{m',m}^{(l)}(-\boldsymbol{\alpha}), \quad (6.35)$$

⁴We will see in chapter 7 that the totality of these states, with integer and half-integer quantum number l , can describe spin states

i.e., $d^{(l)}(\boldsymbol{\alpha})^\dagger d^{(l)}(\boldsymbol{\alpha}) = d^{(l)}(-\boldsymbol{\alpha}) d^{(l)}(\boldsymbol{\alpha}) = 1$, the unit matrix. For given l and $\boldsymbol{\alpha}$, they can be obtained using the relations (5.19) and (5.20) for the angular momentum operators $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$ and \hat{L}_z .

For a rotationally symmetric system, the angular momentum operators $\hat{\mathbf{L}}$ and $\hat{\mathbf{L}}^2$ commute with the Hamilton operator. Therefore, l and m are good quantum numbers. Assuming $|\psi\rangle$ is an energy eigenstate with energy E , then each rotation leads again to an eigenstate with the same energy:

$$\hat{H}|\psi'\rangle = \hat{H}\hat{U}(\boldsymbol{\alpha})|\psi\rangle = \hat{U}(\boldsymbol{\alpha})\underbrace{\hat{U}(\boldsymbol{\alpha})^\dagger \hat{H}\hat{U}(\boldsymbol{\alpha})}_{\hat{H}}|\psi\rangle = \hat{U}(\boldsymbol{\alpha})E|\psi\rangle = E|\psi'\rangle. \quad (6.36)$$

How to determine degeneracy

The degeneracy is determined by the dimension of the representation to which the state belongs. The basis state $|n, l, m\rangle$ (n includes all other quantum numbers defining the state) give a fully orthonormal set of degenerate states with energy $E_{n,l}$. If there are other symmetries beyond the rotation, then the degeneracy is determined by the irreducible representations of the larger symmetry group, e.g. for the Coulomb potential or for the harmonic oscillator. It is not always easy to find all symmetries of a quantum system.

6.4 Discrete transformations: parity and time reversal

The two most important non-continuous symmetry transformations are the *parity* and the *time reversal*. Although both transformations are “inversions” in space and time, respectively, they have different character because in quantum mechanics space and time are treated differently. The position coordinate becomes an operator, the time always remains a parameter.

We consider first parity, i.e., the spatial inversion at the origin: $\mathbf{r} \rightarrow -\mathbf{r}$. We define the parity operator \hat{P} by its action on the position basis:

$$\hat{P}|\mathbf{r}\rangle = |-\mathbf{r}\rangle. \quad (6.37)$$

It follows then, for the action on the momentum basis:

$$\hat{P}|\mathbf{p}\rangle = |-\mathbf{p}\rangle, \quad (6.38)$$

since

$$\begin{aligned} \hat{P}|\mathbf{p}\rangle &= \int d^3r \hat{P}|\mathbf{r}\rangle \langle \mathbf{r}|\mathbf{p}\rangle = \int d^3r |-\mathbf{r}\rangle \langle \mathbf{r}|\mathbf{p}\rangle = \\ &= \int d^3r' |\mathbf{r}'\rangle \langle -\mathbf{r}'|\mathbf{p}\rangle = \int d^3r' |\mathbf{r}'\rangle \langle \mathbf{r}'|-\mathbf{p}\rangle = |-\mathbf{p}\rangle, \end{aligned} \quad (6.39)$$

with the substitution $\mathbf{r}' = -\mathbf{r}$ and the matrix element $\langle \mathbf{r}|\mathbf{p}\rangle = e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}$. For a general state $|\psi\rangle$ with wave function $\psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle$ we get

$$\langle \mathbf{r}|\hat{P}|\psi\rangle = \langle -\mathbf{r}|\psi\rangle = \psi(-\mathbf{r}), \quad (6.40)$$

i.e., the wave function is mirrored at the origin.

One can also easily show that \hat{P} is Hermitian and unitary,

$$\hat{P}^\dagger = \hat{P} = \hat{P}^{-1} \quad \text{and} \quad \hat{P}^\dagger \hat{P} = \hat{P}^2 = \hat{1}, \quad (6.41)$$

and the transformations of position and momentum operators are

$$\hat{P}\hat{\mathbf{r}}\hat{P}^{-1} = \hat{P}\hat{\mathbf{r}}\hat{P} = -\hat{\mathbf{r}} \quad \text{und} \quad \hat{P}\hat{\mathbf{p}}\hat{P}^{-1} = \hat{P}\hat{\mathbf{p}}\hat{P} = -\hat{\mathbf{p}}, \quad (6.42)$$

since, for example, $\hat{P}\hat{\mathbf{r}}\hat{P}|\mathbf{r}\rangle = \hat{P}\hat{\mathbf{r}}|-\mathbf{r}\rangle = -\mathbf{r}\hat{P}|-\mathbf{r}\rangle = -\mathbf{r}|\mathbf{r}\rangle = -\hat{\mathbf{r}}|\mathbf{r}\rangle$. In order for the commutation relation of $\hat{\mathbf{r}}$ with $\hat{\mathbf{p}}$ to remain untouched, \hat{P} has to satisfy the condition

$$\begin{aligned} i\hbar\hat{P}\hat{P}^{-1} &= i\hbar \\ &= [-\hat{x}, -\hat{p}_x] \\ &= [\hat{P}\hat{x}\hat{P}^{-1}, \hat{P}\hat{p}_x\hat{P}^{-1}] \\ &= \hat{P}\hat{x}\hat{P}^{-1}\hat{P}\hat{p}_x\hat{P}^{-1} - \hat{P}\hat{p}_x\hat{P}^{-1}\hat{P}\hat{x}\hat{P}^{-1} \\ &= \hat{P}[\hat{x}, \hat{p}_x]\hat{P}^{-1} \\ &= \hat{P}i\hbar\hat{P}^{-1}. \end{aligned} \quad (6.43)$$

It follows that $\hat{P}i|\psi\rangle = i\hat{P}|\psi\rangle$, i.e. \hat{P} is a linear operator (we will see that this is not the case for the time reversal operator).

We now want to study the eigenvalues ξ and eigenstates $|\psi_\xi\rangle$ of the parity operator,

$$\hat{P}|\psi_\xi\rangle = \xi|\psi_\xi\rangle. \quad (6.44)$$

The parity operator is Hermitian, therefore the eigenvalues are real⁵. The relation $\hat{P}^2 = \hat{1}$ gives

$$\hat{P}^2|\psi_\xi\rangle = \xi^2|\psi_\xi\rangle \stackrel{!}{=} 1|\psi_\xi\rangle, \quad (6.45)$$

i.e., $\xi^2 = 1$: there are only two eigenvalues of \hat{P} , namely $\xi = \pm 1$. Considering the parity transformation of the states (6.40), we see that the eigenvalue +1 corresponds to a state with even wave function, $\psi(-\mathbf{r}) = +\psi(\mathbf{r})$, while the eigenvalue -1 corresponds to a state with odd wave function, $\psi(-\mathbf{r}) = -\psi(\mathbf{r})$.

If the parity represents a symmetry of the system, i.e. the system (the potential) is symmetric under reflection at the origin, then the Hamilton operator commutes with \hat{P} ,

$$[\hat{H}, \hat{P}] = 0. \quad (6.46)$$

Consequently, the eigenstates of \hat{H} can also be chosen to be eigenstates of \hat{P} , even or odd states. This classification of the states facilitates the solution of the Schrödinger equation, as we have already seen in the example of the potential well.

Remark, that the angular momentum operator $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ is invariant under parity:

$$\hat{P}\hat{\mathbf{L}}\hat{P}^{-1} = \hat{P}\hat{\mathbf{L}}\hat{P} = \hat{\mathbf{L}}, \quad \text{equivalent to} \quad [\hat{\mathbf{L}}, \hat{P}] = 0, \quad (6.47)$$

⁵We consider here only the parity of the wave function in position space and neglect the intrinsic parity of a particle.

so that \hat{P} and $\hat{\mathbf{L}}$ can have common eigenstates. For example, the states $|n, l, m\rangle$ of rotationally symmetric systems (like e.g. the hydrogen atom) are eigenstates of \hat{P} with

$$\hat{P}|n, l, m\rangle = (-1)^l |n, l, m\rangle. \quad (6.48)$$

We now come to the time reversal operator \hat{T} . Position and momentum operators transform as follows:

$$\hat{T}\hat{\mathbf{r}}\hat{T}^{-1} = \hat{\mathbf{r}} \quad \text{und} \quad \hat{T}\hat{\mathbf{p}}\hat{T}^{-1} = -\hat{\mathbf{p}}. \quad (6.49)$$

The time reversal $t \rightarrow -t$ thus corresponds to a reversal of the motion. The conservation of the commutation rule for position and momentum operators now shows the difference with respect to \hat{P} :

$$\begin{aligned} -i\hbar\hat{T}\hat{T}^{-1} &= -i\hbar \\ &= [\hat{x}, -\hat{p}_x] \\ &= [\hat{T}\hat{x}\hat{T}^{-1}, \hat{T}\hat{p}_x\hat{T}^{-1}] \\ &= \hat{T}\hat{x}\hat{T}^{-1}\hat{T}\hat{p}_x\hat{T}^{-1} - \hat{T}\hat{p}_x\hat{T}^{-1}\hat{T}\hat{x}\hat{T}^{-1} \\ &= \hat{T}[\hat{x}, \hat{p}_x]\hat{T}^{-1} \\ &= \hat{T}i\hbar\hat{T}^{-1}. \end{aligned} \quad (6.50)$$

It follows that $\hat{T}i|\psi\rangle = -i\hat{T}|\psi\rangle$, i.e., \hat{T} is an antilinear operator:

$$\hat{T}(a_1|\psi_1\rangle + a_2|\psi_2\rangle) = a_1^*\hat{T}|\psi_1\rangle + a_2^*\hat{T}|\psi_2\rangle. \quad (6.51)$$

Applying \hat{T} twice leaves the system invariant, i.e., the states can be at most multiplied by a phase, so that the probabilities remain unchanged. It follows: $\hat{T}^2 = e^{i\alpha}\hat{1}$. The antilinearity gives a condition for the phase:

$$e^{i\alpha}\hat{T}|\psi\rangle = \hat{T}^2\hat{T}|\psi\rangle = \hat{T}\hat{T}^2|\psi\rangle = \hat{T}e^{i\alpha}|\psi\rangle = e^{-i\alpha}\hat{T}|\psi\rangle, \quad (6.52)$$

from which we get $e^{i\alpha} = e^{-i\alpha}$ and thus $e^{i\alpha} = \pm 1$. It can be shown that the sign is related to the angular momentum of the particle:

$$\hat{T}^2 = \begin{cases} +\hat{1}, & \text{integer angular momentum} \\ -\hat{1}, & \text{half-integer angular momentum} \end{cases}. \quad (6.53)$$

A half-integer angular momentum ($l = 1/2, 3/2, \dots$) corresponds to the spin of fermions, as we will see in chapter 7. The orbital angular momentum, on the other hand, can only take integer values ($l = 0, 1, 2, \dots$): we now further consider only this latter case, i.e., the effect of the time reversal operator on the wave functions we have encountered so far.

Time reversal leaves the position basis states invariant:

$$\hat{T}|\mathbf{r}\rangle = |\mathbf{r}\rangle, \quad (6.54)$$

since from (6.49) follows $\hat{T}\hat{\mathbf{r}} = \hat{\mathbf{r}}\hat{T}$ and therefore

$$\hat{\mathbf{r}}\hat{T}|\mathbf{r}\rangle = \hat{T}\hat{\mathbf{r}}|\mathbf{r}\rangle = \hat{T}\mathbf{r}|\mathbf{r}\rangle = \mathbf{r}\hat{T}|\mathbf{r}\rangle, \quad (6.55)$$

i.e., $\hat{T}|\mathbf{r}\rangle$ is also an eigenstate of $\hat{\mathbf{r}}$ with eigenvalue \mathbf{r} . Remark that the eigenvalue is real and therefore it commutes with \hat{T} , without sign change. Analogously, with $\hat{T}\hat{\mathbf{p}} = -\hat{\mathbf{p}}\hat{T}$, we can derive the action on the momentum basis states:

$$\hat{T}|\mathbf{p}\rangle = |-\mathbf{p}\rangle. \quad (6.56)$$

The behavior of the wave function $\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle$ of a general state $|\psi\rangle$ under time reversal is obtained from

$$\hat{T}|\psi\rangle = \int d^3r' \hat{T}\langle \mathbf{r}' | \psi \rangle |\mathbf{r}'\rangle = \int d^3r' \underbrace{\langle \mathbf{r}' | \psi \rangle^*}_{\psi^*(\mathbf{r}')} \hat{T}|\mathbf{r}'\rangle = \int d^3r' \psi^*(\mathbf{r}') |\mathbf{r}'\rangle. \quad (6.57)$$

We find that time reversal for a wave function in the position representation results in the complex conjugation:

$$\langle \mathbf{r} | \hat{T} | \psi \rangle = \psi^*(\mathbf{r}). \quad (6.58)$$

We consider now a system with a time reversal symmetric Hamilton operator, for example $\hat{H} = \hat{\mathbf{p}}^2/2m + V(\hat{\mathbf{r}})$ with a time-independent potential. Then $[\hat{H}, \hat{T}] = 0$ holds and the action of \hat{T} on the Schrödinger equation gives:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H}|\psi(t)\rangle \xrightarrow{\hat{T}} -i\hbar \frac{d}{dt} \hat{T}|\psi(t)\rangle = \hat{H}\hat{T}|\psi(t)\rangle, \quad (6.59)$$

with the change of sign, since \hat{T} anticommutes with i . We see that if $|\psi\rangle$ is a solution, then $\hat{T}|\psi\rangle$ is also a solution, but with a reversed time direction, $t \rightarrow -t$ and $d/dt \rightarrow -d/dt$, as expected:

$$i\hbar \frac{d}{dt} \hat{T}|\psi(-t)\rangle = \hat{H}\hat{T}|\psi(-t)\rangle. \quad (6.60)$$

In the position representation we can then write:

$$i\hbar \frac{d}{dt} \psi^*(\mathbf{r}, -t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi^*(\mathbf{r}, -t), \quad (6.61)$$

i.e., with $\psi(\mathbf{r}, t)$ is also $\psi^*(\mathbf{r}, -t)$ a solution of the Schrödinger equation. We can find this result also by complex conjugation of the Schrödinger equation.

Furthermore, the orbital angular momentum transforms as

$$\hat{T}\hat{\mathbf{L}}\hat{T}^{-1} = -\hat{\mathbf{L}}, \quad (6.62)$$

which can be understood as the reversal of the direction of motion. From this also follows

$$\hat{T}\hat{\mathbf{L}}^2\hat{T}^{-1} = \hat{\mathbf{L}}^2, \quad (6.63)$$

i.e. time reversal leaves the quantum number l of $\hat{\mathbf{L}}^2$ invariant:

$$\hat{\mathbf{L}}^2\hat{T}|l, m\rangle = \hat{T}\hat{\mathbf{L}}^2|l, m\rangle = \hbar^2 l(l+1)\hat{T}|l, m\rangle. \quad (6.64)$$

On the other hand, for $\hat{\mathbf{L}}_z$:

$$\hat{\mathbf{L}}_z\hat{T}|l, m\rangle = -\hat{T}\hat{\mathbf{L}}_z|l, m\rangle = -\hbar m\hat{T}|l, m\rangle, \quad (6.65)$$

i.e., for integer angular momenta, $\hat{T}|l, m\rangle$ is the (normalized) state with quantum numbers l and $-m$:

$$\hat{T}|l, m\rangle = |l, -m\rangle. \quad (6.66)$$

6.5 Gauge invariance

We have seen that the Hamilton operator for a particle with charge q and mass m in an electromagnetic field is given by

$$\hat{H} = \frac{1}{2m} \left(\hat{\mathbf{p}} - \frac{q}{c} \mathbf{A}(\hat{\mathbf{r}}) \right)^2 + q\Phi(\hat{\mathbf{r}}). \quad (6.67)$$

The fields can be expressed using the potentials \mathbf{A} and Φ ,

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} - \nabla \Phi, \quad \mathbf{B} = \nabla \times \mathbf{A}, \quad (6.68)$$

but they still allow a free choice: the gauge transformation

$$\Phi \rightarrow \Phi' = \Phi - \frac{1}{c} \frac{\partial}{\partial t} \chi(\mathbf{r}, t) \quad \text{and} \quad \mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla \chi(\mathbf{r}, t) \quad (6.69)$$

for each function $\chi(\mathbf{r}, t)$ leaves the fields invariant. We now want to study, how this transformation modifies the solutions of the Schrödinger equation and the expectation values of physical quantities.

It turns out that the wave function is only multiplied by a phase factor,

$$\psi(\mathbf{r}, t) \rightarrow \psi'(\mathbf{r}, t) = e^{\frac{iq}{\hbar c} \chi(\mathbf{r}, t)} \psi(\mathbf{r}, t), \quad (6.70)$$

because, if we consider the transformed Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \psi' = \left[\frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{q}{c} \mathbf{A}' \right)^2 + q\Phi' \right] \psi', \quad (6.71)$$

and we insert the transformations (6.69) and (6.70), we get:

$$i\hbar \left(\frac{\partial}{\partial t} - \frac{iq}{\hbar c} \frac{\partial \chi}{\partial t} \right) e^{\frac{iq}{\hbar c} \chi} \psi = \left[\frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{q}{c} \mathbf{A} - \frac{\hbar}{i} \frac{iq}{\hbar c} \nabla \chi \right)^2 + q\Phi \right] e^{\frac{iq}{\hbar c} \chi} \psi. \quad (6.72)$$

The action of the derivatives on the phase factor and division by $e^{iq\chi/\hbar c}$ gives the original (form invariant) Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \psi = \left[\frac{1}{2m} \left(\frac{\hbar}{i} \nabla - \frac{q}{c} \mathbf{A} \right)^2 + q\Phi \right] \psi. \quad (6.73)$$

Notice that the gauge transformation has not changed the physics of the system. The phase of the wave function can not be measured directly, but only bilinear forms $\int d^3r \psi^*(\mathbf{r}) \hat{A}\psi(\mathbf{r})$, in which the phase information is no longer directly visible. Thus, the expectation values of physical quantities are independent of the chosen gauge. We call equation (6.70) a local gauge transformation. The local gauge freedom of the wave function of a charged particle (i.e., the freedom to choose the phase of the wave function) requires the presence of the vector and scalar potentials. The gauge transformations form the continuous Abelian group U(1) of phase transformations of the states and is a fundamental ingredient for the gauge field theories.

Chapter 7

The spin

In addition to the orbital angular momentum, which we have studied in chapter 5, a particle can also have an internal degree of freedom, which behaves like an angular momentum: the spin. The spin is one of the most important properties of a particle, since it determines its statistics (fermionic or bosonic), as we will see in Quantum Mechanics II.

7.1 Stern-Gerlach experiment

At the end of chapter 5 we saw that a charged particle (in an atom or molecule) with a nonvanishing angular momentum quantum number l has a magnetic moment proportional to the angular momentum:

$$\mathbf{M} = \frac{q}{2m_t c} \mathbf{L}, \quad (7.1)$$

where q is the charge and m_t the mass of the particle. For a fixed value of l there exist $2l + 1$ angular momentum states, denoted by the quantum number $m = -l, -l + 1, \dots, l - 1, l$ of the angular momentum component L_z .

On a particle with magnetic moment \mathbf{M} in an inhomogeneous external magnetic field $\mathbf{B} = (0, 0, B_z)$ acts a force \mathbf{F} :

$$\mathbf{F} = \nabla(\mathbf{M} \cdot \mathbf{B}) \approx M_z \nabla B_z = \frac{q}{2m_t c} m \nabla B_z. \quad (7.2)$$

Thus, states with different m experience different strong forces along the gradient of B_z . Stern and Gerlach studied silver atoms (Ag) in this way in 1922. The outer (partially filled) shell of a silver atom has only one 5s-electron and therefore it has a vanishing total orbital angular momentum, i.e. $l = 0$. The Stern-Gerlach experiment was set up in such a way that an Ag atoms beam went through a magnet, which generated an inhomogeneous field (see figure 7.1). With $l = 0$ the atoms should experience no force and reach the screen as a single beam.

What was actually (and unexpectedly) observed, was the splitting of the beam into two components. This does not match any of the possible orbital angular momenta, which all have an odd number of states ($2l + 1$), since l is an integer. The

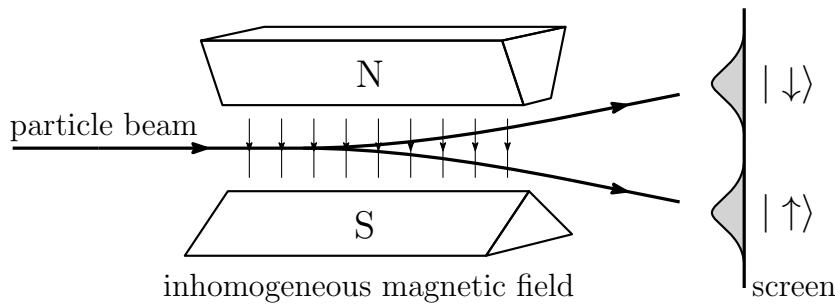


Figure 7.1: Setup of the Stern-Gerlach experiment.

explanation for this discrepancy lies in the fact that the Ag atom has an angular momentum $l = 1/2$ and the quantum number m can take only two values: $\pm 1/2$. This angular momentum can be attributed to the single electron in the 5s level, which has an internal “spin” of $l = 1/2$. Spin is a general property of elementary particles, atoms and also molecules¹.

The Stern-Gerlach experiment is an ideal quantum mechanical measurement process as defined in 3. We perform a measurement at the state

$$|\psi\rangle = a_{+1/2}|1/2, +1/2\rangle + a_{-1/2}|1/2, -1/2\rangle, \quad (7.3)$$

where $|a_{+1/2}|^2 + |a_{-1/2}|^2 = 1$. What we are measuring is an eigenvalue $\hbar m$ of \hat{L}_z . There is a statistical probability that the eigenvalue $\hbar m$ is measured, given by the squared amplitude $|\langle 1/2, m | \psi \rangle|^2 = |a_m|^2$. For each particle there is only one measurement result and its state is fixed after the measurement: if the eigenvalue $\hbar m$ was measured, then the particle is in the state $|1/2, m\rangle$.

7.2 Spin operator and magnetic moment

Analogously to the angular momentum operator we introduce the spin operator $\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$ which has the same commutation relations as $\hat{\mathbf{L}}$,

$$[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}\hat{S}_k, \quad [\hat{S}_z, \hat{S}_\pm] = \pm\hbar\hat{S}_\pm, \quad [\hat{S}_+, \hat{S}_-] = 2\hbar\hat{S}_z, \quad [\hat{\mathbf{S}}^2, \hat{S}_j] = 0, \quad (7.4)$$

where $\hat{\mathbf{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$ and $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$. We can choose any direction \mathbf{e} as the quantization axis ($|\mathbf{e}| = 1$) and consider the spin component $\hat{S}_e = \hat{\mathbf{S}} \cdot \mathbf{e}$. Without restriction of generality, we choose $\mathbf{e} = \mathbf{e}_z$. The considerations of section 5.1 can then be transferred here: since $\hat{\mathbf{S}}^2$ and \hat{S}_z commute, one can find common eigenstates $|s, m\rangle$:

$$\hat{\mathbf{S}}^2|s, m\rangle = \hbar^2 s(s+1)|s, m\rangle, \quad (7.5)$$

$$\hat{S}_z|s, m\rangle = \hbar m|s, m\rangle, \quad (7.6)$$

¹The spin quantum number has an important influence on the behavior of particles, as we will see in Quantum Mechanics II. If the spin quantum number is an integer (like the standard angular momentum), it is called a *boson*. In the half-integer case it is called a *fermion*.

where the quantum number s can now also assume half-integer values ($s = 0, 1/2, 1, 3/2, \dots$) and m can as usual take $2s + 1$ values: $m = -s, -s + 1, \dots, s - 1, s$.

We consider now the (important²) case $s = 1/2$. Then there are two spin eigenstates, with \hat{S}_z eigenvalues $\pm\hbar/2$. We denote these states with $|\uparrow\rangle$ ("spin up") and $|\downarrow\rangle$ ("spin down"),

$$\hat{S}_z |\uparrow\rangle = +\frac{\hbar}{2} |\uparrow\rangle \quad \text{and} \quad \hat{S}_z |\downarrow\rangle = -\frac{\hbar}{2} |\downarrow\rangle. \quad (7.7)$$

They satisfy the orthonormality relations $\langle \uparrow | \downarrow \rangle = 0$ and $\langle \uparrow | \uparrow \rangle = \langle \downarrow | \downarrow \rangle = 1$ and are eigenstates of $\hat{\mathbf{S}}^2$ with eigenvalue $\hbar^2 s(s+1) = 3/4\hbar^2$:

$$\hat{\mathbf{S}}^2 |\uparrow\rangle = \frac{3}{4}\hbar^2 |\uparrow\rangle \quad \text{and} \quad \hat{\mathbf{S}}^2 |\downarrow\rangle = \frac{3}{4}\hbar^2 |\downarrow\rangle. \quad (7.8)$$

The two states $|\uparrow\rangle$ and $|\downarrow\rangle$ are thus an orthonormal basis of the spin-1/2 Hilbert space $\mathcal{H}_{1/2}$. An arbitrary state $|\alpha\rangle \in \mathcal{H}_{1/2}$ (also called *spinor*) can be written as linear combination

$$|\alpha\rangle = \sum_{\sigma=\uparrow,\downarrow} a_\sigma |\sigma\rangle = a_\uparrow |\uparrow\rangle + a_\downarrow |\downarrow\rangle. \quad (7.9)$$

The ladder operators \hat{S}_\pm act in the following way:

$$\hat{S}_+ |\uparrow\rangle = 0, \quad \hat{S}_+ |\downarrow\rangle = \hbar |\uparrow\rangle, \quad \hat{S}_- |\uparrow\rangle = \hbar |\downarrow\rangle, \quad \hat{S}_- |\downarrow\rangle = 0, \quad (7.10)$$

as can be calculated with (5.20).

Since the Hilbert space $\mathcal{H}_{1/2}$ is two-dimensional, one can choose a basis and thereby represent the states as vectors with 2 components and the operators as 2×2 -matrices. For the eigenbasis of \hat{S}_z introduced above we find

$$|\uparrow\rangle \rightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |\downarrow\rangle \rightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (7.11)$$

and thus

$$|\alpha\rangle = a_\uparrow |\uparrow\rangle + a_\downarrow |\downarrow\rangle \rightarrow \begin{pmatrix} a_\uparrow \\ a_\downarrow \end{pmatrix}, \quad (7.12)$$

with the normalization condition $|a_\uparrow|^2 + |a_\downarrow|^2 = 1$. The spin operator is then represented by the *Pauli matrices*³:

$$\hat{\mathbf{S}} \rightarrow \frac{\hbar}{2} \boldsymbol{\sigma} \quad (7.13)$$

with

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (7.14)$$

²Electrons, protons and neutrons have spin $s = 1/2$.

³See appendix D for a summary of the properties of the Pauli matrices.

Note that S_z is diagonal because we choose the quantization axis in z direction. Furthermore, with (7.10), we get

$$S_+ \rightarrow \hbar\sigma_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad S_- \rightarrow \hbar\sigma_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \quad (7.15)$$

for the ladder operators. From these one can get the matrices for $\hat{S}_x = (\hat{S}_+ + \hat{S}_-)/2$ and $\hat{S}_y = (\hat{S}_+ - \hat{S}_-)/2i$.

The action of the spin operator thus corresponds to the multiplication of the matrices with the two-component spinor,

$$\hat{S}_i |\alpha\rangle \rightarrow \frac{\hbar}{2}\sigma_i \begin{pmatrix} a_\uparrow \\ a_\downarrow \end{pmatrix} \quad (7.16)$$

and the expectation values are obtained from the quadratic form

$$\langle \alpha | \hat{S}_i | \alpha \rangle = (a_\uparrow, a_\downarrow)^* \frac{\hbar}{2}\sigma_i \begin{pmatrix} a_\uparrow \\ a_\downarrow \end{pmatrix}. \quad (7.17)$$

Analogously to the orbital angular momentum, the spin generates a magnetic moment:

$$\widehat{\mathbf{M}}_l = \frac{q}{2m_tc} \widehat{\mathbf{L}} \quad \longleftrightarrow \quad \widehat{\mathbf{M}}_s = g_t \frac{q}{2m_tc} \widehat{\mathbf{S}}, \quad (7.18)$$

where g_t is the Landé or gyromagnetic factor of the particle. For an electron it is approximately $g_e \approx 2$ (more precisely $g_e = 2.002319305$) and can be derived from the relativistic description of the electron. The Hamilton operator of the Zeeman effect (see section 5.8) for the total magnetic moment of the electron (with charge $-e$) has then the form

$$\hat{H}_Z = -\widehat{\mathbf{M}}_{tot} \cdot \mathbf{B} = \frac{e}{2m_e c} (\widehat{\mathbf{L}} + 2\widehat{\mathbf{S}}) \cdot \mathbf{B}. \quad (7.19)$$

We notice that the spin quantum number of the electron plays a role in the splitting of the atomic energy levels in a magnetic field.

Also the nuclear particles, proton and neutron, have a spin $s = 1/2$. The magnetic moment of the positively charged proton is approximately three orders of magnitude smaller than that of the electron, because of the mass difference,

$$\widehat{\mathbf{M}}_p = \frac{g_p \mu_p}{\hbar} \widehat{\mathbf{S}} \quad (7.20)$$

with the Bohr's magneton of the proton,

$$\mu_p = \frac{e\hbar}{2m_p c} = 0.505 \times 10^{-23} \frac{\text{erg}}{\text{G}} \approx 10^{-3} \mu_B \quad (7.21)$$

and the gyromagnetic factor $g_p = 5.59$. For the (neutral) neutron

$$\widehat{\mathbf{M}}_n = \frac{g_n \mu_n}{\hbar} \widehat{\mathbf{S}} \quad (7.22)$$

holds, with

$$\mu_n = \frac{e\hbar}{2m_n c}, \quad (7.23)$$

and $g_n = -3.83$. Although the net charge vanishes, the non-uniform charge distribution within the neutron results in a non-vanishing magnetic moment.

7.3 The spinor state

The spin is an internal degree of freedom of a particle and does not depend neither on the spatial coordinates nor on the momentum. Therefore, it commutes with the corresponding operators:

$$[\hat{\mathbf{S}}, \hat{\mathbf{r}}] = [\hat{\mathbf{S}}, \hat{\mathbf{p}}] = [\hat{\mathbf{S}}, \hat{\mathbf{L}}] = 0. \quad (7.24)$$

We therefore distinguish between the *spin* and the *orbital* degrees of freedom.

If a quantum mechanical system has subsystems with independent Hilbert spaces, then the states of the whole system can be written as tensor products of states of the subsystems. As a concrete example we take the *orbital* and *spin* degrees of freedom of an electron with the corresponding Hilbert spaces \mathcal{H}_{orb} and \mathcal{H}_s , respectively. The total Hilbert space is then the tensor product

$$\mathcal{H} = \mathcal{H}_{orb} \otimes \mathcal{H}_s \quad (7.25)$$

with states of the form $|\mathbf{r}\rangle \otimes |\alpha\rangle$ (in the orbital position representation) or $|\mathbf{p}\rangle \otimes |\alpha\rangle$ (in the orbital momentum representation), with $|\alpha\rangle$ a spinor in $\mathcal{H}_{1/2}$. The tensor product of operators acting on the two Hilbert spaces is then understood in the following way:

$$(\hat{A}_{orb} \otimes \hat{A}_s)(|\mathbf{r}\rangle \otimes |\alpha\rangle) = \hat{A}_{orb}|\mathbf{r}\rangle \otimes \hat{A}_s|\alpha\rangle. \quad (7.26)$$

If, for example, the Hamilton operator decomposes into two parts acting separately on the orbital and spin degrees of freedom, then we can write it as

$$\hat{H} = \hat{H}_{orb} \otimes \hat{1}_s + \hat{1}_{orb} \otimes \hat{H}_s, \quad (7.27)$$

where $\hat{1}$ denotes the corresponding identity operator.

The state of a particle can therefore be written as the tensor product of a spin state $|\alpha\rangle = a_\uparrow|\uparrow\rangle + a_\downarrow|\downarrow\rangle$ and an orbital state $\int d^3r \psi(\mathbf{r})|\mathbf{r}\rangle$,

$$|\psi\rangle = \left(\int d^3r \psi(\mathbf{r})|\mathbf{r}\rangle \right) \otimes \left(a_\uparrow|\uparrow\rangle + a_\downarrow|\downarrow\rangle \right) \quad (7.28)$$

$$= \int d^3r \left[(\psi_\uparrow(\mathbf{r})|\mathbf{r}\rangle \otimes |\uparrow\rangle) + (\psi_\downarrow(\mathbf{r})|\mathbf{r}\rangle \otimes |\downarrow\rangle) \right], \quad (7.29)$$

where $\psi_\uparrow(\mathbf{r})$ and $\psi_\downarrow(\mathbf{r})$ represents the wave functions of the spin states:

$$\psi_\sigma(\mathbf{r}) = (\langle \mathbf{r} | \otimes \langle \sigma |) |\psi\rangle = a_\sigma \psi(\mathbf{r}), \quad \sigma = \uparrow, \downarrow. \quad (7.30)$$

The normalization now involves two components:

$$1 = \langle \psi | \psi \rangle = \sum_{\sigma=\uparrow,\downarrow} \int d^3r |\psi_\sigma(\mathbf{r})|^2. \quad (7.31)$$

Thus, one can describe the state of the electron (with charge $-e$) by a spinor (vector) wave function,

$$\Psi(\mathbf{r}) = \begin{pmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{pmatrix}, \quad (7.32)$$

with the Hamilton operator

$$\hat{H} = \frac{1}{2m_e} \left(\hat{\mathbf{p}} + \frac{e}{c} \mathbf{A}(\hat{\mathbf{r}}) \right)^2 - e\Phi(\hat{\mathbf{r}}) + \frac{2\mu_B}{\hbar} \hat{\mathbf{S}} \cdot \mathbf{B}, \quad (7.33)$$

so that the Schrödinger equation is

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}) = \left[\left\{ \frac{1}{2m_e} \left(\frac{\hbar}{i} \nabla + \frac{e}{c} \mathbf{A}(\mathbf{r}) \right)^2 - e\Phi(\mathbf{r}) \right\} \sigma_0 + \mu_B \boldsymbol{\sigma} \cdot \mathbf{B} \right] \Psi(\mathbf{r}), \quad (7.34)$$

with σ_0 the 2×2 unit matrix and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ the Pauli matrices. This is the *Pauli theory* of the electrons. In this equation, the spin and orbital degrees of freedom are independent from each other.

Relativistic corrections, however, can lead to the so-called *spin-orbit coupling*, because the special theory of relativity shows that a charged particle moving in an electric field \mathbf{E} will feel a magnetic field $\mathbf{B} = -(\mathbf{v} \times \mathbf{E})/c$. With the magnetic moment of the electron, $\hat{\mathbf{M}}_e = (-e/m_e c) \hat{\mathbf{S}}$, we get a contribution to the Hamilton operator,

$$\hat{H}_{SB} = -\hat{\mathbf{M}}_e \cdot \mathbf{B} = -\frac{e}{m_e^2 c^2} \hat{\mathbf{S}} \cdot (\hat{\mathbf{p}} \times \mathbf{E}(\hat{\mathbf{r}})). \quad (7.35)$$

Note that for an electron in the electrostatic central potential $V(\mathbf{r}) = V(r) = -e\Phi(r)$ the force is given by

$$\mathbf{F} = -e\mathbf{E} = -\nabla V(\mathbf{r}) = -\frac{\mathbf{r}}{r} \frac{dV}{dr}, \quad (7.36)$$

which gives the Hamilton operator:

$$\hat{H}_{SB} = \frac{1}{m_e^2 c^2} \frac{1}{|\hat{\mathbf{r}}|} \frac{dV}{dr} \hat{\mathbf{S}} \cdot (\hat{\mathbf{r}} \times \hat{\mathbf{p}}) = \frac{1}{m_e^2 c^2} \frac{1}{|\hat{\mathbf{r}}|} \frac{dV}{dr} \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}. \quad (7.37)$$

The prefactor is too large by a factor of 2. This results from the fact that we did not use the inertial frame of the electron in our derivation. If one considers this effect (the Thomas precession), one finally gets

$$\hat{H}_{SB} = \frac{1}{2m_e^2 c^2} \frac{1}{|\hat{\mathbf{r}}|} \frac{dV}{dr} \hat{\mathbf{S}} \cdot \hat{\mathbf{L}}. \quad (7.38)$$

Remark that \hat{H}_{SB} acts as a tensor operator: $\hat{H}_{SB} \propto \sum_{\mu=\{x,y,z\}} \hat{L}_\mu \otimes \hat{S}_\mu$. In Chapter 8 we will discuss the properties and the eigenstates of these operator products.

7.4 Symmetry properties of the spinor states

This is an addendum to the last chapter about symmetries: we now study how the spin states are transformed, under rotations, parity and time reversal.

Analogously to the orbital angular momentum in position space, spin represents the generating operator for rotations in spin space, i.e., rotations of the internal electron degree of freedom, while the orbital degrees of freedom remain untouched.

For a rotation $R(\boldsymbol{\theta})$ in three-dimensional space with rotation angle θ and rotation axis \mathbf{n} ($|\mathbf{n}| = 1$) we introduce the unitary transformation in spinor space

$$\hat{U}_s(\boldsymbol{\theta}) = e^{\frac{i}{\hbar} \boldsymbol{\theta} \cdot \hat{\mathbf{S}}}, \quad (7.39)$$

where $\boldsymbol{\theta} = \theta \mathbf{n}$. Remark that $\hat{U}_s(\boldsymbol{\theta})^\dagger = \hat{U}_s(-\boldsymbol{\theta}) = \hat{U}_s(\boldsymbol{\theta})^{-1}$, i.e., $\hat{U}_s(\boldsymbol{\theta})$ is unitary.

We first consider how the spin operator is rotated: let \mathbf{e} be any quantization axis ($|\mathbf{e}| = 1$) and $\mathbf{e} \cdot \hat{\mathbf{S}}$ be the component of the spin operator in this direction. From (3.47) and the commutation relations (7.4) then follows, for an infinitesimal $\delta\boldsymbol{\theta}$:

$$\begin{aligned} e^{-\frac{i}{\hbar} \delta\boldsymbol{\theta} \cdot \hat{\mathbf{S}}} (\mathbf{e} \cdot \hat{\mathbf{S}}) e^{\frac{i}{\hbar} \delta\boldsymbol{\theta} \cdot \hat{\mathbf{S}}} &= \mathbf{e} \cdot \hat{\mathbf{S}} - \frac{i}{\hbar} [\delta\boldsymbol{\theta} \cdot \hat{\mathbf{S}}, \mathbf{e} \cdot \hat{\mathbf{S}}] + \mathcal{O}(\delta\boldsymbol{\theta}^2) \\ &= \mathbf{e} \cdot \hat{\mathbf{S}} + \sum_{j,k,\ell} \delta\theta_j e_k \epsilon_{jkl} \hat{S}_\ell + \mathcal{O}(\delta\boldsymbol{\theta}^2) \\ &= \mathbf{e} \cdot \hat{\mathbf{S}} + (\delta\boldsymbol{\theta} \times \mathbf{e}) \cdot \hat{\mathbf{S}} + \dots \\ &= (\mathbf{e} + \delta\boldsymbol{\theta} \times \mathbf{e} + \dots) \cdot \hat{\mathbf{S}}, \end{aligned} \quad (7.40)$$

i.e., we get the component of the spin operator in the (infinitesimal) rotated direction $\mathbf{e} + \delta\boldsymbol{\theta} \times \mathbf{e}$. For a general rotation $R(\boldsymbol{\theta})$ we get

$$e^{-\frac{i}{\hbar} \boldsymbol{\theta} \cdot \hat{\mathbf{S}}} (\mathbf{e} \cdot \hat{\mathbf{S}}) e^{\frac{i}{\hbar} \boldsymbol{\theta} \cdot \hat{\mathbf{S}}} = \mathbf{e}' \cdot \hat{\mathbf{S}}, \quad (7.41)$$

where $\mathbf{e}' = R(\boldsymbol{\theta})\mathbf{e}$ is the rotated quantization axis.

If we consider the eigenstate $|\mathbf{e} \uparrow\rangle$ with quantization axis \mathbf{e} , i.e.,

$$(\mathbf{e} \cdot \hat{\mathbf{S}})|\mathbf{e} \uparrow\rangle = +\frac{\hbar}{2}|\mathbf{e} \uparrow\rangle, \quad (7.42)$$

then the transformed state $e^{-i\boldsymbol{\theta} \cdot \hat{\mathbf{S}}/\hbar} |\mathbf{e} \uparrow\rangle$ is an eigenstate of the rotated spin component $\mathbf{e}' \cdot \hat{\mathbf{S}}$, since (with (7.41))

$$(\mathbf{e}' \cdot \hat{\mathbf{S}}) e^{-\frac{i}{\hbar} \boldsymbol{\theta} \cdot \hat{\mathbf{S}}} |\mathbf{e} \uparrow\rangle = e^{-\frac{i}{\hbar} \boldsymbol{\theta} \cdot \hat{\mathbf{S}}} (\mathbf{e} \cdot \hat{\mathbf{S}}) |\mathbf{e} \uparrow\rangle = +\frac{\hbar}{2} e^{-\frac{i}{\hbar} \boldsymbol{\theta} \cdot \hat{\mathbf{S}}} |\mathbf{e} \uparrow\rangle. \quad (7.43)$$

Therefore we find

$$e^{-\frac{i}{\hbar} \boldsymbol{\theta} \cdot \hat{\mathbf{S}}} |\mathbf{e} \uparrow\rangle \propto |\mathbf{e}' \uparrow\rangle \quad \text{and} \quad e^{-\frac{i}{\hbar} \boldsymbol{\theta} \cdot \hat{\mathbf{S}}} |\mathbf{e} \downarrow\rangle \propto |\mathbf{e}' \downarrow\rangle, \quad (7.44)$$

where we only write ‘‘proportional to’’, because the states gain a phase under the transformation, as we will see in a moment.

In the notation of the spinor as a two-component vector we can represent $\hat{U}_s(\boldsymbol{\theta})$ using the Pauli matrices: we get the 2×2 matrix $d_s(\boldsymbol{\theta})$,

$$d_s(\boldsymbol{\theta}) = e^{\frac{i\boldsymbol{\theta} \cdot \boldsymbol{\sigma}}{2}}, \quad (7.45)$$

where $\hat{\mathbf{S}} \rightarrow \frac{\hbar}{2}\boldsymbol{\sigma}$. With equation (D.14) from the appendix we obtain

$$d_s(\boldsymbol{\theta}) = \cos\left(\frac{\theta}{2}\right) \boldsymbol{\sigma}_0 + i \sin\left(\frac{\theta}{2}\right) (\mathbf{n} \cdot \boldsymbol{\sigma}), \quad (7.46)$$

with $d_s(\boldsymbol{\theta})^{-1} = d_s(-\boldsymbol{\theta}) = d_s(\boldsymbol{\theta})^\dagger$.

Applied to the concrete example of a rotation around the z -axis, $\boldsymbol{\varphi} = (0, 0, \varphi)$, we have the matrix representation of $\widehat{U}_s(\boldsymbol{\varphi}) = e^{i\varphi\widehat{S}_z}$:

$$d_s(\boldsymbol{\varphi}) = \cos\left(\frac{\varphi}{2}\right)\sigma_0 + i\sin\left(\frac{\varphi}{2}\right)\sigma_z = \begin{pmatrix} \cos\left(\frac{\varphi}{2}\right) + i\sin\left(\frac{\varphi}{2}\right) & 0 \\ 0 & \cos\left(\frac{\varphi}{2}\right) - i\sin\left(\frac{\varphi}{2}\right) \end{pmatrix}. \quad (7.47)$$

Under such a rotation the spin components $\widehat{S}_i \rightarrow \hbar\sigma_i/2$ (and consequently their expectation values) are transformed as follows:

$$\widehat{S}_x : d_s(-\boldsymbol{\varphi})\frac{\hbar}{2}\sigma_x d_s(\boldsymbol{\varphi}) = \cos(\varphi)\frac{\hbar}{2}\sigma_x + \sin(\varphi)\frac{\hbar}{2}\sigma_y, \quad (7.48)$$

$$\widehat{S}_y : d_s(-\boldsymbol{\varphi})\frac{\hbar}{2}\sigma_y d_s(\boldsymbol{\varphi}) = -\sin(\varphi)\frac{\hbar}{2}\sigma_x + \cos(\varphi)\frac{\hbar}{2}\sigma_y, \quad (7.49)$$

$$\widehat{S}_z : d_s(-\boldsymbol{\varphi})\frac{\hbar}{2}\sigma_z d_s(\boldsymbol{\varphi}) = \frac{\hbar}{2}\sigma_z, \quad (7.50)$$

as one can easily check with matrix multiplication. As expected, the z -component remains unchanged, while the x - and y -components are rotated by the angle φ in the xy -plane: the spin components rotate like a vector.

With the matrix (7.47) we can also see at a simple example how the spinors gain a phase under rotations: the effect of $e^{-i\varphi\widehat{S}_z/\hbar}$ on $|\uparrow\rangle$ corresponds to the multiplication of $d_s(-\boldsymbol{\varphi})$ with the spinor $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$:

$$d_s(-\boldsymbol{\varphi}) \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \left[\cos\left(\frac{\varphi}{2}\right) - i\sin\left(\frac{\varphi}{2}\right) \right] \begin{pmatrix} 1 \\ 0 \end{pmatrix} = e^{-i\frac{\varphi}{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (7.51)$$

i.e., $e^{-i\varphi\widehat{S}_z/\hbar}|\uparrow\rangle = e^{-i\varphi/2}|\uparrow\rangle$. As expected, under rotations around the z -axis, an eigenstate of S_z is not rotated: it is only multiplied by a phase that does not affect the expectation values.

A special property of the rotation of spin $1/2$ states is their *double-valuedness*. From (7.46) we find, in fact, that

$$\begin{aligned} d_s(\boldsymbol{\theta} + 2\pi\mathbf{n}) &= \cos\left(\frac{\theta}{2} + \pi\right)\sigma_0 + i\sin\left(\frac{\theta}{2} + \pi\right)(\mathbf{n} \cdot \boldsymbol{\sigma}) \\ &= -\cos\left(\frac{\theta}{2}\right)\sigma_0 - i\sin\left(\frac{\theta}{2}\right)(\mathbf{n} \cdot \boldsymbol{\sigma}) \\ &= -d_s(\boldsymbol{\theta}), \end{aligned} \quad (7.52)$$

i.e., the rotations $R(\boldsymbol{\theta})$ and $R(\boldsymbol{\theta} + 2\pi\mathbf{n})$, equivalent in position space, gives different matrices in spinor space:

$$d_s(\boldsymbol{\theta}) \quad \text{and} \quad d_s(\boldsymbol{\theta} + 2\pi\mathbf{n}) = -d_s(\boldsymbol{\theta}). \quad (7.53)$$

The spin operator is rotated the same way in both cases, because the transformation matrix occurs 2 times and the minus signs cancel,

$$d_s(\boldsymbol{\theta} + 2\pi\mathbf{n})^{-1} \left(\frac{\hbar}{2} \boldsymbol{\sigma} \cdot \mathbf{e} \right) d_s(\boldsymbol{\theta} + 2\pi\mathbf{n}) = d_s(\boldsymbol{\theta})^{-1} \left(\frac{\hbar}{2} \boldsymbol{\sigma} \cdot \mathbf{e} \right) d_s(\boldsymbol{\theta}). \quad (7.54)$$

On the other hand, all states get a minus sign: e.g. with (7.51) we see that for $\varphi = (0, 0, 2\pi)$,

$$d_s(-\varphi) \begin{pmatrix} 1 \\ 0 \end{pmatrix} = e^{-i\pi} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = - \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \quad (7.55)$$

Only the rotation by $4\pi n$ returns to the same state. This double-valuedness is a general property of half-integer angular momentum and can influence interference properties.

Now we want investigate the discrete transformations: parity and time reversal. The spin operator behaves like the orbital angular momentum under these two transformations. The parity transformation \hat{P} leaves the spin operator invariant, i.e.,

$$\hat{P}^{-1} \hat{S} \hat{P} = \hat{S}. \quad (7.56)$$

On the other hand, for time reversal the transformation is

$$\hat{T}^{-1} \hat{S} \hat{T} = -\hat{S}. \quad (7.57)$$

It is important here to consider the effect of \hat{T} on the spinor. Therefore, we formulate this transformation using Pauli matrices: we can factorize \hat{T} into $\tau \hat{K}$, where τ is a 2×2 matrix and \hat{K} causes the complex conjugation. With the identification $\hat{S} \rightarrow \hbar \sigma / 2$, we get the transformation properties of the Pauli matrices:

$$(\tau \hat{K})^{-1} (\sigma_x, \sigma_y, \sigma_z) (\tau \hat{K}) = (-\sigma_x, -\sigma_y, -\sigma_z). \quad (7.58)$$

Since σ_x and σ_z are real-valued, while σ_y is purely imaginary, the effect of complex conjugation is given by

$$\hat{K}^{-1} (\sigma_x, \sigma_y, \sigma_z) \hat{K} = (\sigma_x, -\sigma_y, \sigma_z). \quad (7.59)$$

It follows that the matrix τ must satisfy the relations:

$$\tau^{-1} (\sigma_x, \sigma_y, \sigma_z) \tau = (-\sigma_x, \sigma_y, -\sigma_z). \quad (7.60)$$

We remark that τ corresponds to a rotation around the y -axis with angle π ,

$$\tau = d_s(\pi \mathbf{e}_y) = e^{\frac{i\pi\sigma_y}{2}} = \cos\left(\frac{\pi}{2}\right) \sigma_0 + i \sin\left(\frac{\pi}{2}\right) \sigma_y = i\sigma_y. \quad (7.61)$$

Therefore we get

$$\hat{T} = e^{\frac{i\pi\sigma_y}{2}} \hat{K} = i\sigma_y \hat{K} \quad (7.62)$$

for a spin-1/2 particle in the spinor representation with two components. It follows:

$$\hat{T}^2 = (i\sigma_y \hat{K})(i\sigma_y \hat{K}) = -\sigma_y^2 = -\sigma_0. \quad (7.63)$$

If we now consider a quantum mechanical system with a time-reversal invariant Hamilton operator and a half-integer angular momentum, then the *Kramer's theorem* holds, which states that all energy eigenvalues are degenerate. Let us namely assume that there is a non-degenerate energy eigenstate $|\psi\rangle$, $\hat{H}|\psi\rangle = E|\psi\rangle$, then this

leads to a contradiction in the following way: because of the time reversal invariance we get

$$\hat{H}\hat{T}|\psi\rangle = \hat{T}\hat{H}|\psi\rangle = E\hat{T}|\psi\rangle. \quad (7.64)$$

Therefore $\hat{T}|\psi\rangle$ must be an eigenstate of \hat{H} with the same energy eigenvalue E . Assuming that this energy eigenvalue is not degenerate, $\hat{T}|\psi\rangle$ must be a multiple of $|\psi\rangle$, i.e., $\hat{T}|\psi\rangle = c|\psi\rangle$. It follows:

$$\hat{T}^2|\psi\rangle = \hat{T}c|\psi\rangle = c^*\hat{T}|\psi\rangle = |c|^2|\psi\rangle. \quad (7.65)$$

But for half-integer angular momenta $\hat{T}^2 = -\hat{1}$ holds and we get a contradiction. Therefore, there are no non-degenerate energy states.

7.5 Spin precession

Spin degrees of freedom have interesting dynamics: let us now study them in more detail. Consider a particle with charge q , mass m , and spin operator $\hat{\mathbf{S}}$ in a homogeneous external magnetic field $\mathbf{B} = (0, 0, B_z)$ in the z direction. Let the particle be fixed in space so that it has no orbital degrees of freedom. Then the Hamilton operator is simply given by

$$?? \quad \hat{H}_s = -\hat{\mathbf{M}}_s \cdot \mathbf{B} = -\frac{gq}{2mc} \hat{\mathbf{S}} \cdot \mathbf{B}, \quad (7.66)$$

with the gyromagnetic factor g . The spin dynamics can be described by the equation of motion for the operators in the Heisenberg representation:

$$\frac{d}{dt} \hat{\mathbf{S}} = -\frac{i}{\hbar} [\hat{\mathbf{S}}, \hat{H}_s] = \frac{gq}{2mc} \hat{\mathbf{S}} \times \mathbf{B}, \quad (7.67)$$

where we used the relation

$$[\hat{S}_i, \hat{S}_j]B_j = i\hbar\epsilon_{ijk}\hat{S}_kB_j = -i\hbar(\hat{\mathbf{S}} \times \mathbf{B})_i. \quad (7.68)$$

It follows:

$$\frac{d}{dt} \hat{S}_x = \omega_0 \hat{S}_y, \quad \frac{d}{dt} \hat{S}_y = -\omega_0 \hat{S}_x, \quad \frac{d}{dt} \hat{S}_z = 0, \quad (7.69)$$

with $\omega_0 = gqB_z/2mc$. The solution gives

$$\hat{S}_x(t) = \hat{S}_x(0) \cos \omega_0 t + \hat{S}_y(0) \sin \omega_0 t, \quad (7.70)$$

$$\hat{S}_y(t) = -\hat{S}_x(0) \sin \omega_0 t + \hat{S}_y(0) \cos \omega_0 t, \quad (7.71)$$

$$\hat{S}_z(t) = \hat{S}_z(0). \quad (7.72)$$

The spin precesses in the magnetic field with angular frequency ω_0 : the so-called *Larmor precession*. For example, if at time $t = 0$ the spin is in x -direction, i.e. $\langle \hat{\mathbf{S}}(0) \rangle = (\hbar/2, 0, 0)$, then the expectation value of the spin operator at time t is

$$\langle \hat{\mathbf{S}}(t) \rangle = \begin{pmatrix} \frac{\hbar}{2} \cos \omega_0 t \\ -\frac{\hbar}{2} \sin \omega_0 t \\ 0 \end{pmatrix}, \quad (7.73)$$

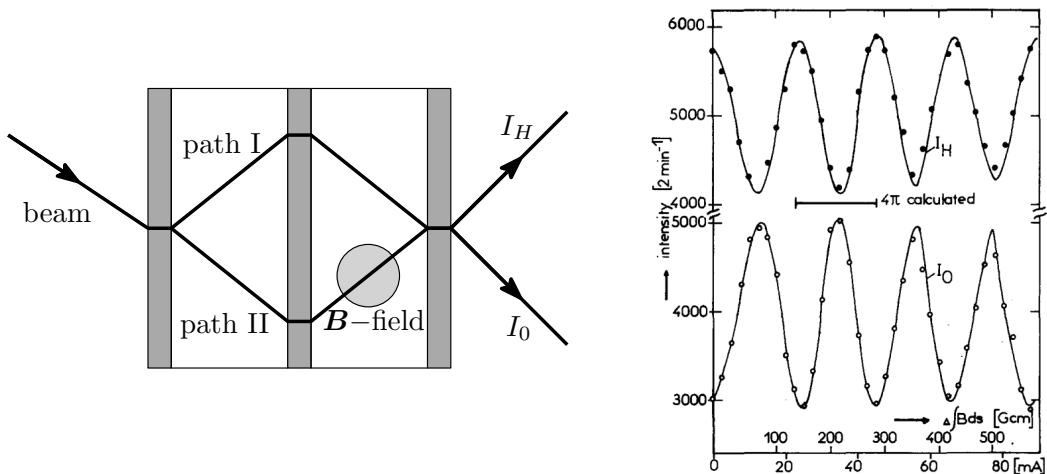


Figure 7.2: Interference effects with neutron spins: the 4π periodicity of intensities follows from the double-valuedness of rotations for half-integer spins.

i.e., the expectation value rotates counterclockwise (for $q > 0$) in the xy -plane. This corresponds, in the Schrödinger representation, to a spin rotation generated by the time evolution of the state:

$$|\Psi(t)\rangle = e^{-\frac{i}{\hbar}\hat{H}_s t}|\Psi(0)\rangle = e^{\frac{i}{\hbar}\omega_0 t \hat{S}_z}|\Psi(0)\rangle. \quad (7.74)$$

One can exploit the Larmor precession to demonstrate the interference effects of the spin-1/2 state. In an experiment with slow neutrons,⁴ a neutron beam is split by Bragg scattering into two separate beams I and II and recombined. (Fig. 7.2). One of the two beams, say II, is exposed to a magnetic field and the spin undergoes a precession. Thus, the subsequent superposition results in an interference effect. Let us assume that the path in the uniform magnetic field B_z has the length ℓ and the neutrons move with the velocity v . Then we find that the interfering final state $|\Psi\rangle_f$ corresponds to the superposition of both paths:

$$|\Psi\rangle_f = |\Psi\rangle_I + |\Psi\rangle_{II} = |\Psi\rangle_i + e^{\frac{i\omega_0\ell}{v\hbar}\hat{S}_z}|\Psi\rangle_i, \quad (7.75)$$

where $|\Psi\rangle_i$ is the initial state. While for $\omega_0\ell/v = 2\pi$ a complete spin rotation is performed, the phase of path II is changed by π and the interference with path I is destructive. Therefore, the period of the interference pattern is $\omega_0\ell/v = 4\pi$. Obviously, the spin has to rotate twice to arrive at the original phase: a nice manifestation of the double-valuedness of the $s = 1/2$ state.

One can also use the Larmor precession to study magnetic properties of materials, using the so-called *muon-spin-rotation* (μ SR)⁵. From the decay product of pions ($\pi^+ \rightarrow \mu^+ + \nu_\mu$) one can obtain 100% spin-polarized muons. The muons have spin quantum number $s = 1/2$. These muons can be injected into materials, where they

⁴S.A. Werner et al., Phys. Rev. Lett. 35, 1053 (1975); H. Rauch et al., Phys. Lett. 54A, 425 (1975),

⁵The μ SR laboratory at the Paul Scherrer Institute in Villigen is world leading in this technique.

are captured in the crystal lattice and their spin precesses in the local magnetic field. The muons decay with a half-life $\tau_\mu = 2.2\mu\text{s}$, and the decay products contain a positron ($\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$), whose preferred emission direction is along the muon spin. Therefore, the detection of the positron allows us to determine the precession angle of the muon spins. In this way, local magnetic fields in a materials can be measured very accurately.

Nuclear spins give another way to determine local magnetic fields in a material very accurately, with the nuclear magnetic resonance (NMR). We consider a nuclear spin with quantum number $s = 1/2$ in a time-dependent magnetic field,

$$\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_1(t) = (B_1 \cos(\omega t), 0, B_0), \quad (7.76)$$

where we apply a stationary field \mathbf{B}_0 along the z axis and an oscillating field \mathbf{B}_1 along the x axis. We consider the time evolution of the spinor state $|\Psi(t)\rangle$ using the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = -\frac{g_N \mu_N}{2} (B_0 \sigma_z + B_1 \cos(\omega t) \sigma_x) |\Psi(t)\rangle, \quad (7.77)$$

with g_N the gyromagnetic factor and μ_N the magneton of the nucleus. We define the modified state $|\Psi'(t)\rangle = e^{-i\omega\sigma_z t/2} |\Psi(t)\rangle$ and we get the equation

$$i \frac{\partial}{\partial t} |\Psi'(t)\rangle = \left[\frac{\omega - \omega_0}{2} \sigma_z - \omega_1 \cos(\omega t) \left(e^{-\frac{i\omega\sigma_z t}{2}} \sigma_x e^{\frac{i\omega\sigma_z t}{2}} \right) \right] |\Psi'(t)\rangle, \quad (7.78)$$

with $\omega_0 = g_N \mu_N B_0 / \hbar$ and $\omega_1 = g_N \mu_N B_1 / 2\hbar$. Now $\sigma_z \sigma_x = -\sigma_x \sigma_z = \sigma_x (-\sigma_z)$ gives $f(\sigma_z) \sigma_x = \sigma_x f(-\sigma_z)$ for each function f . Therefore we get

$$e^{-\frac{i\omega\sigma_z t}{2}} \sigma_x e^{\frac{i\omega\sigma_z t}{2}} = \sigma_x e^{i\omega\sigma_z t} = \sigma_x (\sigma_0 \cos(\omega t) + i\sigma_z \sin(\omega t)). \quad (7.79)$$

With $\cos^2(\alpha) = (\cos(2\alpha) + 1)/2$, $\sin(\alpha) \cos(\alpha) = \sin(2\alpha)/2$ and $\sigma_x \sigma_z = -i\sigma_y$ it follows:

$$i \frac{\partial}{\partial t} |\Psi'(t)\rangle = \left[\frac{\omega - \omega_0}{2} \sigma_z - \frac{\omega_1}{2} \sigma_x - \frac{\omega_1}{2} (\cos(2\omega t) \sigma_x + \sin(2\omega t) \sigma_y) \right] |\Psi'(t)\rangle. \quad (7.80)$$

We neglect the fast-oscillating part and get

$$i \frac{\partial}{\partial t} \langle \uparrow | \Psi'(t) \rangle = \frac{\omega - \omega_0}{2} \langle \uparrow | \Psi'(t) \rangle - \frac{\omega_1}{2} \langle \downarrow | \Psi'(t) \rangle, \quad (7.81)$$

$$i \frac{\partial}{\partial t} \langle \downarrow | \Psi'(t) \rangle = -\frac{\omega_1}{2} \langle \uparrow | \Psi'(t) \rangle - \frac{\omega - \omega_0}{2} \langle \downarrow | \Psi'(t) \rangle. \quad (7.82)$$

This differential equation system can be easily solved by an Ansatz of the form $\langle \sigma | \Psi'(t) \rangle = a_{\sigma,1} \exp(i\Omega t/2) + a_{\sigma,2} \exp(-i\Omega t/2)$ (with $\sigma = \uparrow, \downarrow$). Inserting gives the frequency $\Omega^2 = (\omega - \omega_0)^2 + \omega_1^2$ and an oscillating behavior between the spin states. Let us now assume that at time $t = 0$ the nuclear spin is in state $|\uparrow\rangle$, then we can calculate the probability that at the time t it will be in the state $|\downarrow\rangle$:

$$|\langle \downarrow | \Psi'(t) \rangle|^2 = \frac{\omega_1^2}{\Omega^2} \sin^2 \left(\frac{\Omega t}{2} \right). \quad (7.83)$$

This means that we have a resonance behavior of the amplitude for the “spin flip”. If the oscillating field has just the frequency $\omega = \omega_0$, then $\Omega = \omega_1$: the nuclear spin is reversed with 100% probability at the time $\Delta t = \pi/\omega_1$. The frequency $\omega_0 = g_N \mu_N B_0 / \hbar$ depends, however, on the stationary field B_0 , which can now be measured very accurately using this resonance. In this way, local fields or susceptibilities in materials can be determined very accurately. NMR is one of the most important measurement methods in solid state physics and biophysics for the investigation of local magnetic properties of materials.

Chapter 8

Addition of angular momenta

In atomic, nuclear and particle physics as in other many-particle problems often situations arise in which two or more coupled angular momentum degrees of freedom occur. Then it is better to work no longer with the individual angular momenta, but to use the total angular momentum. This is called the addition of angular momenta, i.e., if $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ are two angular momentum operators of a quantum system ($\hat{\mathbf{J}}_i$ can be the orbital angular momentum or spin of the same particle or of different particles), then

$$\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 \quad (8.1)$$

is the total angular momentum. Obviously $\hat{\mathbf{J}}$ also satisfies the commutation relations of an angular momentum and has corresponding eigenstates. The states of the system with two angular momenta can be expressed with the help of product states of the form

$$|j_1, m_1; j_2, m_2\rangle := |j_1, m_1\rangle \otimes |j_2, m_2\rangle, \quad (8.2)$$

where

$$\hat{\mathbf{J}}_i^2 |j_i, m_i\rangle = \hbar^2 j_i(j_i + 1) |j_i, m_i\rangle \quad \text{and} \quad \hat{J}_{i,z} |j_i, m_i\rangle = \hbar m_i |j_i, m_i\rangle \quad (8.3)$$

hold. However, such product states are not eigenstates of the total angular momentum operator $\hat{\mathbf{J}}$. If the two angular momentum degrees of freedom are coupled, then there is no longer an independent rotational symmetry for $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$, but in general only the complete rotational symmetry, where all degrees of freedom are simultaneously rotated. These rotations are generated by $\hat{\mathbf{J}}$. It is therefore mandatory to work in the basis of the total angular momentum since this corresponds to a constant of the motion and determines the good quantum numbers. In this chapter, we will introduce the formalism that allows us to deal with the addition of angular momenta.

8.1 Two spin 1/2 degrees of freedom

An illustrative example is the addition of two spin 1/2 degrees of freedom $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ with $[\hat{S}_{1,\mu}, \hat{S}_{2,\nu}] = 0$ (for $\mu, \nu = x, y, z$). We choose as basis of each spin space the

eigenstates of $\hat{S}_{i,z}$ (i.e. $|\uparrow\rangle_i$ and $|\downarrow\rangle_i$) and write the product states in short notation,

$$|\uparrow\uparrow\rangle = |\uparrow\rangle_1 \otimes |\uparrow\rangle_2, \quad |\uparrow\downarrow\rangle = |\uparrow\rangle_1 \otimes |\downarrow\rangle_2, \quad |\downarrow\uparrow\rangle = |\downarrow\rangle_1 \otimes |\uparrow\rangle_2, \quad |\downarrow\downarrow\rangle = |\downarrow\rangle_1 \otimes |\downarrow\rangle_2, \quad (8.4)$$

as our basis states. This means that the Hilbert space \mathcal{D} , which includes both spins, is four-dimensional:

$$\mathcal{D} = \mathcal{D}_{\frac{1}{2}} \otimes \mathcal{D}_{\frac{1}{2}}. \quad (8.5)$$

The total spin is defined as

$$\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2, \quad (8.6)$$

the sum¹ of both spin 1/2 operators $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$. Now we want to determine the eigenstates $|s, m\rangle$ of the total spin in this Hilbert space, i.e.,

$$\hat{\mathbf{S}}^2 |s, m\rangle = \hbar^2 s(s+1) |s, m\rangle \quad \text{and} \quad \hat{S}_z |s, m\rangle = \hbar m |s, m\rangle. \quad (8.7)$$

For the product states we have:

$$\hat{S}_z |\uparrow\uparrow\rangle = (\hat{S}_{1,z} + \hat{S}_{2,z}) |\uparrow\uparrow\rangle = \left(\frac{\hbar}{2} + \frac{\hbar}{2}\right) |\uparrow\uparrow\rangle = \hbar |\uparrow\uparrow\rangle, \quad (8.8)$$

$$\hat{S}_z |\downarrow\downarrow\rangle = (\hat{S}_{1,z} + \hat{S}_{2,z}) |\downarrow\downarrow\rangle = \left(-\frac{\hbar}{2} - \frac{\hbar}{2}\right) |\downarrow\downarrow\rangle = -\hbar |\downarrow\downarrow\rangle, \quad (8.9)$$

$$\hat{S}_z |\uparrow\downarrow\rangle = (\hat{S}_{1,z} + \hat{S}_{2,z}) |\uparrow\downarrow\rangle = \left(\frac{\hbar}{2} - \frac{\hbar}{2}\right) |\uparrow\downarrow\rangle = 0, \quad (8.10)$$

$$\hat{S}_z |\downarrow\uparrow\rangle = (\hat{S}_{1,z} + \hat{S}_{2,z}) |\downarrow\uparrow\rangle = \left(-\frac{\hbar}{2} + \frac{\hbar}{2}\right) |\downarrow\uparrow\rangle = 0, \quad (8.11)$$

i.e., they are all eigenstates of \hat{S}_z . However, this is not the case for $\hat{\mathbf{S}}^2$. With the ladder operators $\hat{S}_{i,\pm} = \hat{S}_{i,x} \pm i\hat{S}_{i,y}$ we can write $\hat{\mathbf{S}}^2$ as

$$\hat{\mathbf{S}}^2 = \hat{\mathbf{S}}_1^2 + \hat{\mathbf{S}}_2^2 + 2\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \hat{\mathbf{S}}_1^2 + \hat{\mathbf{S}}_2^2 + \hat{S}_{1,+}\hat{S}_{2,-} + \hat{S}_{1,-}\hat{S}_{2,+} + 2\hat{S}_{1,z}\hat{S}_{2,z}. \quad (8.12)$$

Since

$$\hat{S}_{i,+} |\uparrow\uparrow\rangle = \hat{S}_{i,-} |\downarrow\downarrow\rangle = 0, \quad i = 1, 2, \quad (8.13)$$

we get

$$\begin{aligned} \hat{\mathbf{S}}^2 |\uparrow\uparrow\rangle &= (\hat{\mathbf{S}}_1^2 + \hat{\mathbf{S}}_2^2 + 2\hat{S}_{1,z}\hat{S}_{2,z}) |\uparrow\uparrow\rangle \\ &= \left(\frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2 + 2\frac{1}{4}\hbar^2\right) |\uparrow\uparrow\rangle \\ &= 2\hbar^2 |\uparrow\uparrow\rangle, \end{aligned} \quad (8.14)$$

and analogously

$$\hat{\mathbf{S}}^2 |\downarrow\downarrow\rangle = 2\hbar^2 |\downarrow\downarrow\rangle. \quad (8.15)$$

¹More precisely, the total spin should be written as the tensor operator $\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 \otimes \hat{1} + \hat{1} \otimes \hat{\mathbf{S}}_2$, where $\hat{\mathbf{S}}_1$ acts on the first, while $\hat{\mathbf{S}}_2$ on the second spin.

Therefore they are both eigenstates of $\hat{\mathbf{S}}^2$ and \hat{S}_z , which can be identified with $|s, m\rangle$,

$$|1, +1\rangle = |\uparrow\uparrow\rangle \quad \text{and} \quad |1, -1\rangle = |\downarrow\downarrow\rangle, \quad (8.16)$$

i.e., they belong to the spin Hilbert space \mathcal{D}_1 with $s = 1$. The third basis state in this space is obtained with the action of the lowering operator $\hat{S}_- = \hat{S}_{1,-} + \hat{S}_{2,-}$ on $|1, 1\rangle$: on the one hand, with (5.20),

$$\hat{S}_-|1, 1\rangle = \sqrt{2}\hbar|1, 0\rangle, \quad (8.17)$$

on the other hand,

$$\hat{S}_-|1, 1\rangle = (\hat{S}_{1,-} + \hat{S}_{2,-})|\uparrow\uparrow\rangle = \hbar(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle). \quad (8.18)$$

Thus, the basis of the three-dimensional Hilbert space \mathcal{D}_1 is:

$$|1, +1\rangle = |\uparrow\uparrow\rangle, \quad (8.19)$$

$$|1, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \quad (8.20)$$

$$|1, -1\rangle = |\downarrow\downarrow\rangle. \quad (8.21)$$

Now there is still the possibility to write a second state with eigenvalue 0 for \hat{S}_z as a linear combination of $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$. The only combination that is orthogonal to $|1, 0\rangle$ is $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$. From

$$(\hat{S}_{1,-}\hat{S}_{2,+} + \hat{S}_{1,+}\hat{S}_{2,-})(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = \hbar^2(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle) = -\hbar^2(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (8.22)$$

and (8.12) follows that this state is an eigenstate of $\hat{\mathbf{S}}^2$ with eigenvalue 0:

$$\hat{\mathbf{S}}^2(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = \hbar^2\left(\frac{3}{4} + \frac{3}{4} - 1 + 2\frac{-1}{4}\right)(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) = 0. \quad (8.23)$$

We thus have

$$|0, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (8.24)$$

as basis of the one-dimensional Hilbert space \mathcal{D}_0 with $s = 0$.

In representation theory, every Hilbert space \mathcal{D}_s corresponds to a representation and one speaks of the decomposition of the tensor product of representations (Hilbert spaces):

$$\mathcal{D}_{\frac{1}{2}} \otimes \mathcal{D}_{\frac{1}{2}} = \mathcal{D}_0 \oplus \mathcal{D}_1, \quad ? \quad (8.25)$$

i.e., the combination of two spin $1/2$ gives one state with angular momentum $s = 0$ (singlet) and three states with angular momentum $s = 1$ (triplet). Notice that for the dimensions of the involved Hilbert spaces the relation

$$2 \cdot 2 = \dim(\mathcal{D}_{\frac{1}{2}}) \cdot \dim(\mathcal{D}_{\frac{1}{2}}) = \dim(\mathcal{D}_0) + \dim(\mathcal{D}_1) = 1 + 3 = 4, \quad (8.26)$$

holds, with $\dim(\mathcal{D}_l) = 2l + 1$.

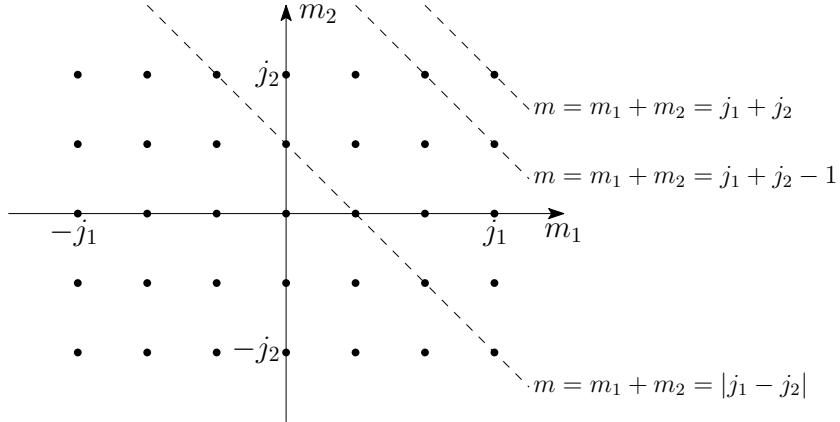


Figure 8.1: Representation of the product states $|j_1, m_1; j_2, m_2\rangle$ in the m_1, m_2 -plane.

In magnetic systems, spin interactions often appear as coupling between spins, which have the form $\hat{H} = \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$ (a so-called exchange interaction). The basis states of the total spin are also eigenstates of this operator, since from (8.12) follows

$$\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \frac{1}{2} \left(\hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_2^2 \right), \quad (8.27)$$

where both operators $\hat{\mathbf{S}}_i^2$ have the eigenvalue $3\hbar^2/4$ for spin $s = 1/2$. Therefore, we find

$$\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 |s, m\rangle = \frac{1}{2}\hbar^2 \left[s(s+1) - \frac{3}{2} \right] |s, m\rangle = \begin{cases} -\frac{3}{4}\hbar^2 |0, 0\rangle & \text{singlet} \\ +\frac{1}{4}\hbar^2 |1, m\rangle & \text{triplet} \end{cases}. \quad (8.28)$$

Obviously, only the total spin yields good quantum numbers here, since the Hamilton operator \hat{H} is only invariant under the simultaneous rotation of both spins (of the total spin), but not of each spin separately.

8.2 General case: addition of two angular momenta

We consider now $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$, two angular momentum operators which commute with each other. Thus we can write a complete basis of product states (eigenstates of both operators): $|j_1, m_1; j_2, m_2\rangle$. With fixed j_1 and j_2 we can represent these states as points in a m_1, m_2 -diagram, as shown in Figure 8.1, where the dashed diagonals correspond to the states with constant $m_1 + m_2$. If in the Hamilton operator there is a coupling between these angular momenta, then m_1 and m_2 are no longer good quantum numbers, as we saw in the previous section with the coupling of two spins, and we must again consider the total angular momentum, $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$. The good quantum numbers are j_1, j_2, j and m for the operators $\hat{\mathbf{J}}_1^2, \hat{\mathbf{J}}_2^2, \hat{\mathbf{J}}^2$ and \hat{J}_z , respectively. These operators all commute with each other, therefore the corresponding eigenstates $|j_1, j_2; j, m\rangle$ are a complete basis.

All states of this new basis are orthogonal to each other and are normalized. We also note, that the old and new basis contain the same number of states. We can

check this as follows. Let us assume $j_1 \geq j_2$. There is a product state $|j_1, m_1; j_2, m_2\rangle$ with $m_1 = j_1$ and $m_2 = j_2$. It is also an eigenstate of \hat{J}_z with $m = m_1 + m_2 = j_1 + j_2$, so that $j = j_1 + j_2$ is the maximal quantum number of the total angular momentum. Then there are also two product states with $m = m_1 + m_2 = j_1 + j_2 - 1$: $|j_1, j_1; j_2, j_2 - 1\rangle$ and $|j_1, j_1 - 1; j_2, j_2\rangle$ (as in Figure 8.1). There are two orthogonal linear combinations of these states: one belongs to $j = j_1 + j_2$, while the other to $j = j_1 + j_2 - 1$. If $j_2 > 1/2$, then there are also states with smaller values of j , where $j = j_1 - j_2$ is the smallest value that can be reached. Since for each j there are $2j + 1$ states, it follows that the number of basis states $|j_1, j_2; j, m\rangle$ is²

$$\sum_{j=j_1-j_2}^{j_1+j_2} (2j + 1) = (2j_1 + 1)(2j_2 + 1), \quad (8.29)$$

as claimed. This corresponds to the decomposition

$$\mathcal{D}_{j_1} \otimes \mathcal{D}_{j_2} = \mathcal{D}_{|j_1-j_2|} \oplus \mathcal{D}_{|j_1-j_2|+1} \oplus \cdots \oplus \mathcal{D}_{j_1+j_2-1} \oplus \mathcal{D}_{j_1+j_2}, \quad (8.30)$$

so that

$$\dim(\mathcal{D}_{j_1}) \cdot \dim(\mathcal{D}_{j_2}) = \sum_{j=|j_1-j_2|}^{j_1+j_2} \dim(\mathcal{D}_j). \quad (8.31)$$

Now we want to study the basis transformation,

$$|j_1, j_2; j, m\rangle = \sum_{m_1, m_2} |j_1, m_1; j_2, m_2\rangle \langle j_1, m_1; j_2, m_2 | j_1, j_2; j, m\rangle, \quad (8.32)$$

and vice versa,

$$|j_1, m_1; j_2, m_2\rangle = \sum_{j, m} |j_1, j_2; j, m\rangle \langle j_1, j_2; j, m | j_1, m_1; j_2, m_2\rangle, \quad (8.33)$$

where both sums are limited to $m_1 + m_2 = m$. The so-called *Clebsch-Gordan coefficients* $\langle j_1, m_1; j_2, m_2 | j_1, j_2; j, m\rangle$ gives the unitary transformation.

Here are some properties of these coefficients. We will use the short notation $|m_1, m_2\rangle = |j_1, m_1; j_2, m_2\rangle$ and $|j, m\rangle = |j_1, j_2; j, m\rangle$ from now on, since j_1 and j_2 are fixed. The following orthogonality relations

$$\langle m_1, m_2 | m'_1, m'_2 \rangle = \sum_{j, m} \langle m_1, m_2 | j, m \rangle \langle j, m | m'_1, m'_2 \rangle = \delta_{m_1, m'_1} \delta_{m_2, m'_2}, \quad (8.34)$$

$$\langle j, m | j', m' \rangle = \sum_{m_1, m_2} \langle j, m | m_1, m_2 \rangle \langle m_1, m_2 | j', m' \rangle = \delta_{j, j'} \delta_{m, m'}, \quad (8.35)$$

hold, with $m = m_1 + m_2$. Furthermore, all Clebsch-Gordan coefficients can be chosen to be real:

$$\langle j, m | m_1, m_2 \rangle = \langle m_1, m_2 | j, m \rangle. \quad (8.36)$$

²For an arithmetic succession a_k the sum formula $\sum_{k=n}^m a_k = (a_n + a_m)(m - n + 1)/2$ holds.

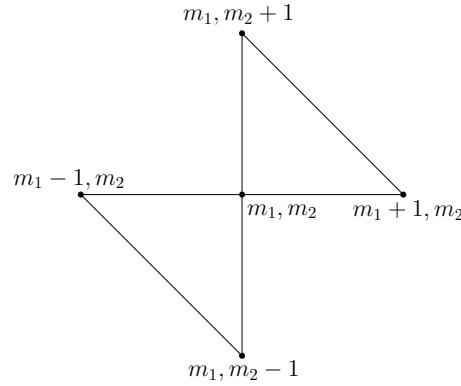


Figure 8.2: Diagrammatic representation of the relations (8.37) and (8.38) in the m_1, m_2 -plane: bottom left for \hat{J}_+ , top right for \hat{J}_- .

We can compute all coefficients using recursion relations. Namely, for $\hat{J}_{\pm} = \hat{J}_{1,\pm} + \hat{J}_{2,\pm}$ the matrix elements

$$\langle m_1, m_2 | \hat{J}_{\pm} | j, m \rangle = \sqrt{j(j+1) - m(m \pm 1)} \langle m_1, m_2 | j, m \pm 1 \rangle \quad (8.37)$$

and

$$\begin{aligned} \langle m_1, m_2 | \hat{J}_{1,\pm} + \hat{J}_{2,\pm} | j, m \rangle &= \sqrt{j_1(j_1+1) - m_1(m_1 \mp 1)} \langle m_1 \mp 1, m_2 | j, m \rangle \\ &\quad + \sqrt{j_2(j_2+1) - m_2(m_2 \mp 1)} \langle m_1, m_2 \mp 1 | j, m \rangle \end{aligned} \quad (8.38)$$

hold. If we equate the two equations (8.37) and (8.38), we obtain a relation between three different coefficients for the quantum number j . One can represent these relations with triangles in the m_1, m_2 -plane, as shown in Fig. 8.2. If we know two of the coefficients, then from the triangle relations we can compute the third one.

Our task is to determine for fixed but arbitrary j with $|j_1 - j_2| \leq j \leq j_1 + j_2$ the coefficients $\langle m_1, m_2 | j, m \rangle$ for all m_1, m_2 in the white area of Figure 8.3 (m is determined by $m = m_1 + m_2$). For this goal, we start at the point marked with

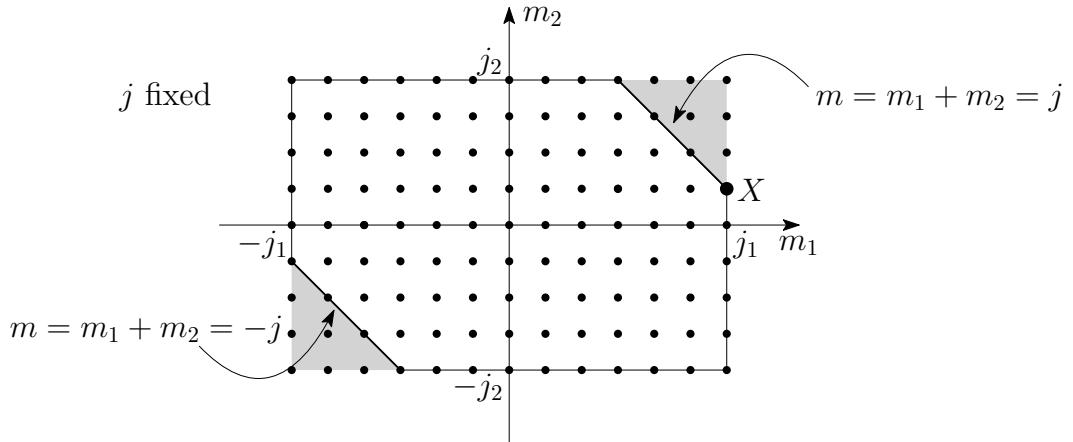


Figure 8.3: Diagram for the computation of the Clebsch-Gordan coefficients.

X and choose the corresponding coefficient $\langle j_1, j - j_1 | j, j \rangle = \lambda \in \mathbb{R}$. Using the triangular relations, one can now determine all other coefficients as a function of λ (where the coefficients corresponding to points outside the white area are equal to 0). Using the orthogonality condition (8.35) (with $j' = j$ and $m' = m$), one can also determine λ at the end. We will not go into further details here and just give the table of the most important Clebsch-Gordan coefficients for integer and half-integer angular momenta (Fig. 8.4).

A case, which occurs frequently in practice, is the addition of an angular momentum with quantum number j_1 to a spin $s = 1/2$. The result is

$$\mathcal{D}_{j_1} \otimes \mathcal{D}_{\frac{1}{2}} = \mathcal{D}_{j_1 + \frac{1}{2}} \oplus \mathcal{D}_{j_1 - \frac{1}{2}} \quad (8.39)$$

and the Clebsch-Gordan coefficients $\langle j_1, m_1; \frac{1}{2}, m_2 | j_1, \frac{1}{2}; j, m \rangle$ with $m = m_1 + m_2$ are given by

	$m_2 = +\frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j = j_1 + \frac{1}{2}$	$\sqrt{\frac{j_1+m+1/2}{2j_1+1}}$	$\sqrt{\frac{j_1-m+1/2}{2j_1+1}}$
$j = j_1 - \frac{1}{2}$	$-\sqrt{\frac{j_1-m+1/2}{2j_1+1}}$	$\sqrt{\frac{j_1+m+1/2}{2j_1+1}}$

8.3 Tensor operators

We now consider the properties of the so-called irreducible tensor operators, which in many aspects show analogies with angular momentum properties. We will show that due to symmetry considerations, matrix elements of tensor operators have certain universal properties.

Irreducible tensor operators are operators acting on a Hilbert space, which exhibit the following transformation behavior under rotations. We define a tensor operator $\hat{T}_{k,q}$ of order k , belonging to an irreducible set of $2k + 1$ operators with $q = -k, -k + 1, \dots, k - 1, k$. The rotation transformation

$$\hat{U}(\boldsymbol{\alpha}) = e^{\frac{i}{\hbar} \hat{\boldsymbol{J}} \cdot \boldsymbol{\alpha}} \quad (8.40)$$

is defined by means of the total angular momentum $\hat{\boldsymbol{J}}$ of the quantum system and acts on $\hat{T}_{k,q}$ by a linear transformation in the irreducible operator space:

$$\hat{U}(\boldsymbol{\alpha}) \hat{T}_{k,q} \hat{U}(\boldsymbol{\alpha})^\dagger = \sum_{q'=-k}^{+k} d_{q',q}^{(k)}(\boldsymbol{\alpha}) \hat{T}_{k,q'}, \quad (8.41)$$

where the transformation matrices are identical to the matrices for the transformation of angular momentum eigenstates from section 6.3:

$$\hat{U}(\boldsymbol{\alpha}) |k, q\rangle = \sum_{q'} d_{q',q}^{(k)}(\boldsymbol{\alpha}) |k, q'\rangle. \quad (8.42)$$

45. Clebsch-Gordan Coefficients, Spherical Harmonics, and d Functions

Note: A square-root sign is to be understood over *every* coefficient, e.g., for $-8/15$ read $-\sqrt{8/15}$. Notation:

J	J	...
M	M	...
m_1	m_2	
\vdots	\vdots	
		Coefficients

$Y_\ell^0 = \sqrt{\frac{3}{4\pi}} \cos \theta$

$Y_1^0 = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}$

$Y_2^0 = \sqrt{\frac{5}{4\pi}} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)$

$Y_1^1 = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi}$

$Y_2^1 = \frac{1}{4\sqrt{2\pi}} \sin^2 \theta e^{2i\phi}$

$3/2 \times 1/2$

$Y_\ell^{-m} = (-1)^m Y_\ell^{m*}$

$d_{m,0}^\ell = \sqrt{\frac{4\pi}{2\ell+1}} Y_\ell^m e^{-im\phi}$

$\langle j_1 j_2 m_1 m_2 | j_1 j_2 JM \rangle$

$= (-1)^{J-j_1-j_2} \langle j_2 j_1 m_2 m_1 | j_2 j_1 JM \rangle$

$d_{m',m}^j = (-1)^{m-m'} d_{m',m}^j = d_{-m,-m'}^j$

$3/2 \times 3/2$

$d_{1,0}^1 = \cos \theta$

$d_{1/2,1/2}^{1/2} = \cos \frac{\theta}{2}$

$d_{1,1}^1 = \frac{1 + \cos \theta}{2}$

$d_{1/2,-1/2}^{1/2} = -\sin \frac{\theta}{2}$

$d_{1,0}^1 = -\frac{\sin \theta}{\sqrt{2}}$

$d_{1,-1}^1 = \frac{1 - \cos \theta}{2}$

$2 \times 3/2$

$d_{1,0}^2 = \cos \theta$

$d_{1/2,1/2}^{1/2} = \cos \frac{\theta}{2}$

$d_{1,1}^2 = \frac{1 + \cos \theta}{2}$

$d_{1/2,-1/2}^{1/2} = -\sin \frac{\theta}{2}$

$d_{1,0}^2 = -\frac{\sin \theta}{\sqrt{2}}$

$d_{1,-1}^2 = \frac{1 - \cos \theta}{2}$

2×2

$d_{1,0}^3 = \cos \theta$

$d_{1/2,1/2}^{1/2} = \cos \frac{\theta}{2}$

$d_{1,1}^3 = \frac{1 + \cos \theta}{2}$

$d_{1/2,-1/2}^{1/2} = -\sin \frac{\theta}{2}$

$d_{1,0}^3 = -\frac{\sin \theta}{\sqrt{2}}$

$d_{1,-1}^3 = \frac{1 - \cos \theta}{2}$

$d_{3/2,3/2}^{1/2} = \frac{1 + \cos \theta}{2} \cos \frac{\theta}{2}$

$d_{3/2,1/2}^{1/2} = -\sqrt{3} \frac{1 + \cos \theta}{2} \sin \frac{\theta}{2}$

$d_{3/2,-1/2}^{1/2} = \sqrt{3} \frac{1 - \cos \theta}{2} \cos \frac{\theta}{2}$

$d_{3/2,-3/2}^{1/2} = -\frac{1 - \cos \theta}{2} \sin \frac{\theta}{2}$

$d_{1/2,1/2}^{1/2} = \frac{3 \cos \theta - 1}{2} \cos \frac{\theta}{2}$

$d_{1/2,-1/2}^{1/2} = -\frac{3 \cos \theta + 1}{2} \sin \frac{\theta}{2}$

$d_{3/2,3/2}^{3/2} = \frac{1 + \cos \theta}{2} \cos \frac{\theta}{2}$

$d_{3/2,1/2}^{3/2} = \frac{1 + \cos \theta}{2} \sin \frac{\theta}{2}$

$d_{3/2,-1/2}^{3/2} = -\frac{1 + \cos \theta}{2} \sin \frac{\theta}{2}$

$d_{3/2,-3/2}^{3/2} = \frac{\sqrt{6}}{4} \sin^2 \theta$

$d_{1/2,1/2}^{3/2} = -\frac{1 - \cos \theta}{2} \sin \theta$

$d_{1/2,-1/2}^{3/2} = -\frac{1 - \cos \theta}{2} \sin \theta$

$d_{3/2,3/2}^{5/2} = \frac{1 + \cos \theta}{2} (2 \cos \theta - 1)$

$d_{3/2,1/2}^{5/2} = \frac{1 - \cos \theta}{2} (2 \cos \theta + 1)$

$d_{3/2,-1/2}^{5/2} = \frac{1 - \cos \theta}{2} (2 \cos \theta + 1)$

$d_{3/2,-3/2}^{5/2} = \frac{3}{2} \cos^2 \theta - \frac{1}{2}$

Figure 45.1: The sign convention is that of Wigner (*Group Theory*, Academic Press, New York, 1959), also used by Condon and Shortley (*The Theory of Atomic Spectra*, Cambridge Univ. Press, New York, 1953), Rose (*Elementary Theory of Angular Momentum*, Wiley, New York, 1957), and Cohen (*Tables of the Clebsch-Gordan Coefficients*, North American Rockwell Science Center, Thousand Oaks, Calif., 1974).

Figure 8.4: Clebsch-Gordan coefficients, from P.A. Zyla et al. (Particle Data Group), Prog. Theor. Exp. Phys. 2020, 083C01 (2020).

It follows then:

$$d_{q',q}^{(k)}(\boldsymbol{\alpha}) = \langle k, q' | \widehat{U}(\boldsymbol{\alpha}) | k, q \rangle, \quad (8.43)$$

i.e., this is the irreducible representation of rotations in the Hilbert space \mathcal{D}_k . If, on the contrary, the rotation representation is reducible, the tensor operator is also called reducible.

If we consider an infinitesimal transformation $\widehat{U}(\delta\boldsymbol{\alpha})$, then in first order with respect to $\delta\boldsymbol{\alpha}$ the left hand side of the condition (8.41) is

$$\left(\widehat{1} + \frac{i}{\hbar} \widehat{\mathbf{J}} \cdot \delta\boldsymbol{\alpha} \right) \widehat{T}_{k,q} \left(\widehat{1} - \frac{i}{\hbar} \widehat{\mathbf{J}} \cdot \delta\boldsymbol{\alpha} \right) = \widehat{T}_{k,q} + \frac{i}{\hbar} \delta\boldsymbol{\alpha} \cdot [\widehat{\mathbf{J}}, \widehat{T}_{k,q}], \quad (8.44)$$

and the right hand side

$$\sum_{q'=-k}^{+k} \langle k, q' | \widehat{1} + \frac{i}{\hbar} \widehat{\mathbf{J}} \cdot \delta\boldsymbol{\alpha} | k, q \rangle \widehat{T}_{k,q'} = \widehat{T}_{k,q} + \frac{i}{\hbar} \delta\boldsymbol{\alpha} \cdot \sum_{q'=-k}^{+k} \langle k, q' | \widehat{\mathbf{J}} | k, q \rangle \widehat{T}_{k,q'}. \quad (8.45)$$

A comparison of the coefficients gives a condition equivalent to (8.41):

$$[\widehat{\mathbf{J}}, \widehat{T}_{k,q}] = \sum_{q'=-k}^{+k} \langle k, q' | \widehat{\mathbf{J}} | k, q \rangle \widehat{T}_{k,q'}. \quad (8.46)$$

The z component of this equation is then

$$[\widehat{J}_z, \widehat{T}_{k,q}] = \sum_{q'=-k}^{+k} \langle k, q' | \widehat{J}_z | k, q \rangle \widehat{T}_{k,q'} = \hbar q \widehat{T}_{k,q}, \quad (8.47)$$

while

$$[\widehat{J}_{\pm}, \widehat{T}_{k,q}] = \sum_{q'=-k}^{+k} \langle k, q' | \widehat{J}_{\pm} | k, q \rangle \widehat{T}_{k,q'} = \hbar \sqrt{k(k+1) - q(q \pm 1)} \widehat{T}_{k,q \pm 1}. \quad (8.48)$$

A scalar operator, invariant under rotations, has order $k = 0$ and corresponds thus to the trivial (one-dimensional) representation: $d_{0,0}^{(0)}(\boldsymbol{\alpha}) = 1$. A Vector operator (like for example position and momentum operators) or pseudo vector operator (like for example the angular momentum operator) $\widehat{\mathbf{V}} = (\widehat{V}_x, \widehat{V}_y, \widehat{V}_z)$ satisfies the commutation relations

$$[\widehat{J}_i, \widehat{V}_j] = i\hbar \epsilon_{ij\ell} \widehat{V}_\ell, \quad i, j = x, y, z, \quad (8.49)$$

(with summation over ℓ) and is a tensor operator with order $k = 1$ and components

$$\widehat{T}_{1,+1} = \widehat{V}_{+1} = -\frac{\widehat{V}_x + i\widehat{V}_y}{\sqrt{2}}, \quad \widehat{T}_{1,0} = \widehat{V}_0 = \widehat{V}_z, \quad \widehat{T}_{1,-1} = \widehat{V}_{-1} = \frac{\widehat{V}_x - i\widehat{V}_y}{\sqrt{2}}, \quad (8.50)$$

as one can verify using (8.47) and (8.48).

8.4 Wigner-Eckart theorem

We investigate now the state resulting from the application of a tensor operator $\hat{T}_{k,q}$ to the state $|n_1, j_1, m_1\rangle$ (n_1 includes all other quantum numbers besides the angular momentum quantum numbers). First we consider the properties of this state under rotations $\hat{U}(\boldsymbol{\alpha})$:

$$\begin{aligned}\hat{U}(\boldsymbol{\alpha})\hat{T}_{k,q}|n_1, j_1, m_1\rangle &= \hat{U}(\boldsymbol{\alpha})\hat{T}_{k,q}\hat{U}(\boldsymbol{\alpha})^\dagger\hat{U}(\boldsymbol{\alpha})|n_1, j_1, m_1\rangle \\ &= \sum_{q',m'} d_{q',q}^{(k)}(\boldsymbol{\alpha})d_{m'm_1}^{(j_1)}(\boldsymbol{\alpha})\hat{T}_{k,q'}|n_1, j_1, m'\rangle.\end{aligned}\quad (8.51)$$

We remark that the state $\hat{T}_{k,q}|n_1, j_1, m_1\rangle$ transforms like a product state of the form $|k, q\rangle \otimes |j_1, m_1\rangle$. We consider now a rotation around the z axis, $\boldsymbol{\alpha} = (0, 0, \varphi)$. For the corresponding transformation matrix we get $d_{q',q}^{(k)}(\boldsymbol{\alpha}) = \delta_{q,q'}e^{iq\varphi}$. Therefore, it follows:

$$\hat{U}(\boldsymbol{\alpha})\hat{T}_{k,q}|n_1, j_1, m_1\rangle = e^{i(q+m_1)\varphi}\hat{T}_{k,q}|n_1, j_1, m_1\rangle. \quad (8.52)$$

This means that the state $\hat{T}_{k,q}|n_1, j_1, m_1\rangle$ is an eigenstate of \hat{J}_z with eigenvalue $\hbar(q + m_1)$, but it is not an eigenstate of $\hat{\mathbf{J}}^2$.

However, the action of a tensor operator $\hat{T}_{k,q}$ on an angular momentum eigenstate $|n_1, j_1, m_1\rangle$ is analogous to the addition of two angular momenta with quantum numbers k, q and j_1, m_1 , respectively, and we can generate eigenstates of $\hat{\mathbf{J}}^2$ and \hat{J}_z using the Clebsch-Gordan coefficients:

$$|\tilde{n}_1, j, m\rangle = \sum_{q,m_1} \hat{T}_{k,q}|n_1, j_1, m_1\rangle\langle k, q; j_1, m_1|k, j_1; j, m\rangle, \quad (8.53)$$

and vice versa

$$\hat{T}_{k,q}|n_1, j_1, m_1\rangle = \sum_{m,j} |\tilde{n}_1, j, m\rangle\langle k, j_1; j, m|k, q; j_1, m_1\rangle, \quad (8.54)$$

where the sums are restricted to the terms with $m = q + m_1$ and \tilde{n}_1 denotes the action of the operator on the other degrees of freedom of the state: \tilde{n}_1 does not need to be a quantum number, but only corresponds to an index of the state.

Now we can formulate the *Wigner-Eckart theorem*: the matrix elements of tensor operators can be written in the form:

$$\langle n_2, j_2, m_2|\hat{T}_{k,q}|n_1, j_1, m_1\rangle = \frac{\langle n_2, j_2||\hat{T}_k||n_1, j_1\rangle}{\sqrt{2j_2+1}}\langle k, j_1; j_2, m_2|k, q; j_1, m_1\rangle, \quad (8.55)$$

where $\langle n_2, j_2||\hat{T}_k||n_1, j_1\rangle$ is the so-called reduced matrix element, which depends only on n_1, j_1, n_2, j_2 and k (the denominator $\sqrt{2j_2+1}$ is a convention), while the dependence on the quantum numbers m_1, m_2 and q is fully encoded in the Clebsch-Gordan coefficient $\langle k, j_1; j_2, m_2|k, q; j_1, m_1\rangle$, with $m_1 + q = m_2$.

We prove the theorem first for a scalar operator \hat{T}_0 (i.e., $k = 0$), which per definition commutes with the angular momentum operator and with all rotation transformations: $[\hat{T}_0, \hat{\mathbf{J}}] = 0$ and $[\hat{T}_0, \hat{U}(\boldsymbol{\alpha})] = 0$. From (8.54) follows that $\hat{T}_0|n_1, j_1, m_1\rangle = |\tilde{n}_1, j_1, m_1\rangle$ is also an eigenstate of $\hat{\mathbf{J}}^2$ and \hat{J}_z . Thus:

$$\langle n_2, j_2, m_2 | \hat{T}_0 | n_1, j_1, m_1 \rangle = t(n_2, j_2, m_2; n_1, j_1, m_1) \delta_{j_1, j_2} \delta_{m_1, m_2}, \quad (8.56)$$

i.e., the matrix element vanishes if $j_1 \neq j_2$ and/or $m_1 \neq m_2$. However if $j_1 = j_2$ and $m_1 = m_2$, then

$$\begin{aligned} t(n_2, j_1, m_1 - 1; n_1, j_1, m_1 - 1) &= \langle n_2, j_1, m_1 - 1 | \hat{T}_0 | n_1, j_1, m_1 - 1 \rangle \\ &= \frac{\langle n_2, j_1, m_1 | \hat{J}_+ \hat{T}_0 \hat{J}_- | n_1, j_1, m_1 \rangle}{j_1(j_1 + 1) - m_1(m_1 - 1)} \\ &= \frac{\langle n_2, j_1, m_1 | \hat{T}_0 \hat{J}_+ \hat{J}_- | n_1, j_1, m_1 \rangle}{j_1(j_1 + 1) - m_1(m_1 - 1)} \quad (8.57) \\ &= \langle n_2, j_1, m_1 | \hat{T}_0 | n_1, j_1, m_1 \rangle \\ &= t(n_2, j_1, m_1; n_1, j_1, m_1), \end{aligned}$$

holds, i.e., the matrix element t does not depend on m_1 and we can write

$$\langle n_2, j_2, m_2 | \hat{T}_0 | n_1, j_1, m_1 \rangle = \underbrace{\frac{\langle n_2, j_2 | \hat{T}_0 | n_1, j_1 \rangle}{\sqrt{2j_2 + 1}}}_{t(n_2, j_2; n_1, j_1)} \underbrace{\langle 0, j_1; j_2, m_2 | 0, 0; j_1, m_1 \rangle}_{\delta_{j_1, j_2} \delta_{m_1, m_2}}. \quad (8.58)$$

In this case the Wigner-Eckart theorem is satisfied.

We extend now the discussion to the general case of the tensor operator $\hat{T}_{k,q}$. From (8.54) follows

$$\langle n_2, j_2, m_2 | \hat{T}_{k,q} | n_1, j_1, m_1 \rangle = \sum_{m,j} \langle n_2, j_2, m_2 | \tilde{n}_1, j, m \rangle \langle k, j_1; j, m | k, q; j_1, m_1 \rangle. \quad (8.59)$$

For $\langle n_2, j_2, m_2 | \tilde{n}_1, j, m \rangle$ we can now use (8.58) ($\hat{1}$ is a scalar operator) and we get the claim of the Wigner-Eckart theorem:

$$\begin{aligned} \langle n_2, j_2, m_2 | \hat{T}_{k,q} | n_1, j_1, m_1 \rangle &= \sum_{m,j} t(n_2, j_2; \tilde{n}_1, j) \delta_{j_1, j_2} \delta_{m_1, m_2} \langle k, j_1; j, m | k, q; j_1, m_1 \rangle \\ &= \underbrace{t(n_2, j_2; \tilde{n}_1, j_2)}_{\frac{\langle n_2, j_2 | \hat{T}_k | n_1, j_1 \rangle}{\sqrt{2j_2 + 1}}} \langle k, j_1; j_2, m_2 | k, q; j_1, m_1 \rangle. \quad (8.60) \end{aligned}$$

Note that even in systems with imperfect rotational symmetry (e.g., in the crystal lattice of a solid), an adapted formulation of the same theorem is still possible.

Applying the Wigner-Eckart theorem to an arbitrary tensor operator \hat{V} of order $k = 1$ provides a useful relation that we will use later to compute expectation values. Since the total angular momentum $\hat{\mathbf{J}}$ is also such an operator of order $k = 1$, it

follows from the Wigner-Eckart theorem that their matrix elements in a subspace $\mathcal{U}_{n,j}$ with fixed $n_1 = n_2 = n$ and $j_1 = j_2 = j$ are proportional to each other:

$$\begin{aligned}\langle n, j, m_2 | \hat{\mathbf{V}}_q | n, j, m_1 \rangle &= \frac{\langle n, j | \hat{\mathbf{V}} | n, j \rangle}{\sqrt{2j+1}} \langle 1, j; j, m_2 | 1, q; j, m_1 \rangle \\ &= \underbrace{\frac{\langle n, j | \hat{\mathbf{V}} | n, j \rangle}{\langle n, j | \hat{\mathbf{J}} | n, j \rangle}}_{\alpha(n, j)} \langle n, j, m_2 | \hat{\mathbf{J}}_q | n, j, m_1 \rangle,\end{aligned}\quad (8.61)$$

i.e., restricted on this subspace the relation $\hat{\mathbf{V}}|_{\mathcal{U}_{n,j}} = \alpha(n, j) \hat{\mathbf{J}}|_{\mathcal{U}_{n,j}}$ holds. Therefore we also have

$$\hat{\mathbf{V}} \cdot \hat{\mathbf{J}}|_{\mathcal{U}_{n,j}} = \alpha(n, j) \hat{\mathbf{J}}^2|_{\mathcal{U}_{n,j}} = \alpha(n, j) \hbar^2 j(j+1) \quad (8.62)$$

and we find

$$\alpha(n, j) = \frac{\hat{\mathbf{V}} \cdot \hat{\mathbf{J}}|_{\mathcal{U}_{n,j}}}{\hbar^2 j(j+1)}. \quad (8.63)$$

The insertion in (8.61) gives the useful relation

$$\langle n, j, m_2 | \hat{\mathbf{V}} | n, j, m_1 \rangle = \frac{\langle n, j | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | n, j \rangle}{\hbar^2 j(j+1)} \langle n, j, m_2 | \hat{\mathbf{J}} | n, j, m_1 \rangle, \quad (8.64)$$

which, from linearity, is also valid for the cartesian components of the operators.

Finally, we consider an example that illustrates the selection rules for the matrix elements of tensor operators of the form $\langle n_2, j_2, m_2 | \hat{T}_{k,q} | n_1, j_1, m_1 \rangle$. As an example, we consider the tensor operator of order $k = 1$. From the Wigner-Eckart theorem we can conclude in general that non-vanishing matrix elements are possible under the condition

$$|j_1 - k| \leq j_2 \leq j_1 + k \quad \text{and} \quad q + m_1 = m_2, \quad (8.65)$$

from which, with $k = 1$ and $q = 0, \pm 1$ it follows, that

$$j_2 - j_1 = 0, \pm 1 \quad \text{und} \quad m_2 - m_1 = 0, \pm 1. \quad (8.66)$$

Otherwise, the Clebsch-Gordan coefficients vanish.

If we consider tensor operators of order $k = 1$, we can derive further constraints on the matrix elements. On the one hand we already know the vector operator $\hat{\mathbf{V}}$. On the other hand there are also tensor operators corresponding to a pseudovector, e.g. the angular momentum $\hat{\mathbf{J}}$. Vector and pseudovector operators have the same behavior under rotation: they are both tensor operators of order $k = 1$. The difference lies in their behavior under the parity transformation:

$$\hat{P} \hat{\mathbf{V}} \hat{P} = -\hat{\mathbf{V}} \quad \text{and} \quad \hat{P} \hat{\mathbf{J}} \hat{P} = \hat{\mathbf{J}}. \quad (8.67)$$

The matrix elements of $\hat{\mathbf{V}}$ have thus the following property:

$$\langle n_2, j_2, m_2 | \hat{\mathbf{V}} | n_1, j_1, m_1 \rangle = -\langle n_2, j_2, m_2 | \hat{P} \hat{\mathbf{V}} \hat{P} | n_1, j_1, m_1 \rangle \quad (8.68)$$

$$= -(-1)^{j_1+j_2} \langle n_2, j_2, m_2 | \hat{\mathbf{V}} | n_1, j_1, m_1 \rangle, \quad (8.69)$$

because of the parity property 6.48 of the angular momentum eigenstates. It follows that for a non-vanishing matrix element the condition $j_2 = j_1 \pm 1$ is necessary, i.e. $j_2 = j_1$ is not possible. For the pseudovector operator $\hat{\mathbf{J}}$ the analogous reasoning gives that

$$\langle n_2, j_2, m_2 | \hat{\mathbf{J}} | n_1, j_1, m_1 \rangle = \langle n_2, j_2, m_2 | \hat{P} \hat{\mathbf{J}} \hat{P} | n_1, j_1, m_1 \rangle \quad (8.70)$$

$$= (-1)^{j_1+j_2} \langle n_2, j_2, m_2 | \hat{\mathbf{J}} | n_1, j_1, m_1 \rangle. \quad (8.71)$$

In order for the matrix element not to vanish, $j_1 = j_2$ must hold.

Thus, in summary:

$$\langle n_2, j_2, m_2 | \hat{\mathbf{V}} | n_1, j_1, m_1 \rangle \neq 0 \quad \text{for } j_2 = j_1 \pm 1, m_2 - m_1 = 0, \pm 1, \quad (8.72)$$

$$\langle n_2, j_2, m_2 | \hat{\mathbf{J}} | n_1, j_1, m_1 \rangle \neq 0 \quad \text{for } j_2 = j_1, m_2 - m_1 = 0, \pm 1. \quad (8.73)$$

As we will see in Quantum Mechanics II, these properties correspond to the selection rules for optical transitions in atoms. The vector operator has the symmetry of an electric dipole and the pseudo vector operator has the symmetry of a magnetic dipole.

Chapter 9

Approximation methods

Many quantum mechanical systems lead to mathematical problems which cannot be solved exactly or only with great effort. In such cases numerical methods are often used. But there are also approximation methods that allow an analytical insight into a problem. Here we will consider the perturbation theory, the variational approximation and the WKB method.

9.1 Rayleigh-Schrödinger perturbation theory

We assume that the Hamilton operator can be written as a sum of two terms

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad (9.1)$$

where all eigenstates $|\varphi_n\rangle$ and energy eigenvalues ε_n of \hat{H}_0 are exactly known,

$$\hat{H}_0|\varphi_n\rangle = \varepsilon_n|\varphi_n\rangle, \quad (9.2)$$

and constitute an orthonormal basis of the considered Hilbert space. How will the eigenstates and the energy eigenvalues change under the influence of \hat{V} ? We naturally consider the case with $[\hat{V}, \hat{H}_0] \neq 0$, otherwise the problem would be almost trivial. As first we restrict our study to non-degenerate states, i.e. $\varepsilon_n \neq \varepsilon_m$ for $n \neq m$. We introduce a small parameter λ and write

$$\hat{H} = \hat{H}_0 + \lambda\hat{V}, \quad (9.3)$$

where λ can vary between 0 and 1. Then we can write the corrected eigenstates $|\psi_n\rangle$ and energy eigenvalues E_n as power series in the small parameter λ :

$$|\psi_n\rangle = |\varphi_n\rangle + \lambda|\phi_n^{(1)}\rangle + \lambda^2|\phi_n^{(2)}\rangle + \dots \quad (9.4)$$

$$E_n = \varepsilon_n + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (9.5)$$

The existence of such an expansion presupposes that there is a one-to-one mapping between the old and the new spectrum. This is not automatically the case. In particular, it is not possible to move from bound to extended (unbound) states and

vice versa. We will limit our discussion to states belonging to a discrete energy spectrum.

In a first step, we ignore the default normalization of the new state and assume $\langle \varphi_n | \psi_n \rangle = 1$, where of course $\langle \varphi_n | \varphi_n \rangle = 1$ should also hold. The relation

$$1 = \langle \varphi_n | \psi_n \rangle = \underbrace{\langle \varphi_n | \varphi_n \rangle}_1 + \lambda \langle \varphi_n | \phi_n^{(1)} \rangle + \lambda^2 \langle \varphi_n | \phi_n^{(2)} \rangle + \dots \quad (9.6)$$

requires that $\langle \varphi_n | \phi_n^{(k)} \rangle = 0$. We insert (9.4) and (9.5) in the eigenvalue equation

$$(\hat{H}_0 + \lambda \hat{V}) |\psi_n\rangle = E_n |\psi_n\rangle. \quad (9.7)$$

Since this equation must hold for any value of λ , we can perform a coefficient comparison in any power of λ . At zero-th order, we find the eigenvalue equation (9.2). The first order in λ leads to the equation

$$\hat{H}_0 |\phi_n^{(1)}\rangle + \hat{V} |\varphi_n\rangle = \varepsilon_n |\phi_n^{(1)}\rangle + E_n^{(1)} |\varphi_n\rangle. \quad (9.8)$$

The k -th power of λ gives the equation

$$\hat{H}_0 |\phi_n^{(k)}\rangle + \hat{V} |\phi_n^{(k-1)}\rangle = \varepsilon_n |\phi_n^{(k)}\rangle + \sum_{j=1}^{k-1} E_n^{(j)} |\phi_n^{(k-j)}\rangle + E_n^{(k)} |\varphi_n\rangle. \quad (9.9)$$

We now project these equations onto the state $|\varphi_n\rangle$ and calculate the corrections for the energy. From (9.8) follows

$$\underbrace{\langle \varphi_n | \hat{H}_0 | \phi_n^{(1)} \rangle}_{\varepsilon_n \langle \varphi_n | \phi_n^{(1)} \rangle = 0} + \langle \varphi_n | \hat{V} | \varphi_n \rangle = \varepsilon_n \underbrace{\langle \varphi_n | \phi_n^{(1)} \rangle}_0 + E_n^{(1)} \quad (9.10)$$

and we get:

$$E_n^{(1)} = \langle \varphi_n | \hat{V} | \varphi_n \rangle, \quad (9.11)$$

i.e., the first order correction of the energy is simply given by the expectation value of the perturbation \hat{V} in the unperturbed state $|\varphi_n\rangle$. The higher order corrections give analogously

$$E_n^{(k)} = \langle \varphi_n | \hat{V} | \phi_n^{(k-1)} \rangle, \quad (9.12)$$

where here the $k-1$ -th order correction of the state is needed.

The corrections of the states can be expressed using the old eigenstates,

$$|\phi_n^{(k)}\rangle = \sum_{m \neq n} |\varphi_m\rangle \langle \varphi_m | \phi_n^{(k)} \rangle, \quad (9.13)$$

where the sum runs only over $m \neq n$, since $\langle \varphi_n | \phi_n^{(k)} \rangle = 0$. We get the coefficients $\langle \varphi_m | \phi_n^{(k)} \rangle$ with the projection of (9.9) on $|\varphi_m\rangle$:

$$\underbrace{\langle \varphi_m | \hat{H}_0 | \phi_n^{(k)} \rangle}_{\varepsilon_m \langle \varphi_m | \phi_n^{(k)} \rangle} + \langle \varphi_m | \hat{V} | \phi_n^{(k-1)} \rangle = \varepsilon_n \langle \varphi_m | \phi_n^{(k)} \rangle + \sum_{j=1}^{k-1} E_n^{(j)} \langle \varphi_m | \phi_n^{(k-j)} \rangle, \quad (9.14)$$

from which it follows:

$$\langle \varphi_m | \phi_n^{(k)} \rangle = \frac{1}{\varepsilon_n - \varepsilon_m} \left(\langle \varphi_m | \hat{V} | \phi_n^{(k-1)} \rangle - \sum_{j=1}^{k-1} E_n^{(j)} \langle \varphi_m | \phi_n^{(k-j)} \rangle \right), \quad (9.15)$$

where $|\phi_n^{(0)}\rangle \equiv |\varphi_n\rangle$ for $k = 1$. The equations (9.12) and (9.15) give a system of equations, which allows the iterative determination of the corrections for all orders.

We give here explicitly the corrections for the two lowest and most important orders. For the first order we get

$$E_n^{(1)} = \langle \varphi_n | \hat{V} | \varphi_n \rangle, \quad (9.16)$$

$$|\phi_n^{(1)}\rangle = \sum_{m \neq n} |\varphi_m\rangle \frac{\langle \varphi_m | \hat{V} | \varphi_n \rangle}{\varepsilon_n - \varepsilon_m}, \quad (9.17)$$

and for the second order

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \varphi_n | \hat{V} | \varphi_m \rangle|^2}{\varepsilon_n - \varepsilon_m}, \quad (9.18)$$

$$|\phi_n^{(2)}\rangle = \sum_{m \neq n} \sum_{k \neq n} |\varphi_m\rangle \frac{\langle \varphi_m | \hat{V} | \varphi_k \rangle \langle \varphi_k | \hat{V} | \varphi_n \rangle}{(\varepsilon_n - \varepsilon_k)(\varepsilon_n - \varepsilon_m)} - \sum_{m \neq n} |\varphi_m\rangle \frac{\langle \varphi_m | \hat{V} | \varphi_n \rangle \langle \varphi_n | \hat{V} | \varphi_n \rangle}{(\varepsilon_n - \varepsilon_m)^2}. \quad (9.19)$$

The states $|\varphi_k\rangle$ which occur here are called virtual states or intermediate states. The perturbation allows the quantum system to briefly reside in other eigenstates, violating the conservation of energy. Because of the energy-time uncertainty relation this is not a problem.

The new eigenstate $|\psi_n\rangle$ is not yet normalized, i.e., $\langle \psi_n | \psi_n \rangle \neq 1$. We now want to get the right normalization. If $\langle \psi_n | \psi_n \rangle = 1/Z_n$ then $|\bar{\psi}_n\rangle = \sqrt{Z_n} |\psi_n\rangle$ is normalized, i.e., $\langle \bar{\psi}_n | \bar{\psi}_n \rangle = 1$. Thus we need to determine Z_n :

$$\langle \psi_n | \psi_n \rangle = \left(\langle \varphi_n | + \sum_{k=1}^{\infty} \lambda^k \langle \phi_n^{(k)} | \right) \left(|\varphi_n\rangle + \sum_{k'=1}^{\infty} \lambda^{k'} |\phi_n^{(k')}\rangle \right) = 1 + \sum_{\ell=2}^{\infty} \lambda^{\ell} \sum_{j=1}^{\ell-1} \langle \phi_n^{(\ell-j)} | \phi_n^{(j)} \rangle \quad (9.20)$$

gives up to second order

$$\langle \psi_n | \psi_n \rangle = 1 + \lambda^2 \sum_{m \neq n} \frac{|\langle \varphi_m | \hat{V} | \varphi_n \rangle|^2}{(\varepsilon_n - \varepsilon_m)^2} + \dots, \quad (9.21)$$

from which it follows, with the geometric series $(1-x)^{-1} = 1 + x + \dots$,

$$Z_n = 1 - \lambda^2 \sum_{m \neq n} \frac{|\langle \varphi_m | \hat{V} | \varphi_n \rangle|^2}{(\varepsilon_n - \varepsilon_m)^2} + \dots. \quad (9.22)$$

This corresponds to

$$Z_n = \frac{\partial}{\partial \varepsilon_n} \left(\varepsilon_n + \lambda \langle \varphi_n | \hat{V} | \varphi_n \rangle + \lambda^2 \sum_{m \neq n} \frac{|\langle \varphi_m | \hat{V} | \varphi_n \rangle|^2}{\varepsilon_n - \varepsilon_m} + \dots \right) = \frac{\partial E_n}{\partial \varepsilon_n}. \quad (9.23)$$

This means that Z_n is the partial derivative of E_n with respect to ε_n , where all ε_m (for $m \neq n$) and matrix elements remain constant. This holds for all orders in λ , which we will not prove here. Besides the renormalization, Z_n also has the meaning of the probability to find the original state $|\varphi_n\rangle$ in the corrected state $|\bar{\psi}_n\rangle$, i.e.,

$$|\langle \varphi_n | \bar{\psi}_n \rangle|^2 = Z_n \underbrace{|\langle \varphi_n | \psi_n \rangle|^2}_1 = Z_n. \quad (9.24)$$

9.2 Applications of perturbation theory: the harmonic oscillator with a constant force

We now consider an example, which we can solve both approximately and exactly. This is the one-dimensional harmonic oscillator with a constant force F ,

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 \quad \text{and} \quad \hat{V} = -F\hat{x}. \quad (9.25)$$

The exact solution can be simply found by completing the square:

$$\hat{H} = \hat{H}_0 + \hat{V} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2} \left(\hat{x} - \frac{F}{m\omega^2} \right)^2 - \frac{F^2}{2m\omega^2}, \quad (9.26)$$

which corresponds to a harmonic oscillator with an equilibrium point shifted by $F/m\omega^2$ and with an energy shifted by $-F^2/2m\omega^2$. The energy eigenvalues and the corresponding eigenstates are

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) - \frac{F^2}{2m\omega^2} \quad \text{and} \quad |\bar{\psi}_n\rangle = e^{-\frac{i\hat{p}F}{m\omega^2\hbar}} |\varphi_n\rangle, \quad (9.27)$$

where the new eigenstate $|\bar{\psi}_n\rangle$ is simply the translation of the eigenstate $|\varphi_n\rangle$ of \hat{H}_0 .

Now we consider the perturbative approach. The unperturbed states are the eigenstates $|\varphi_n\rangle$ of the harmonic oscillator, with energy eigenvalues $\varepsilon_n = \hbar\omega(n+1/2)$. To determine the matrix elements $\langle \varphi_m | \hat{V} | \varphi_n \rangle$, we need to consider representation of \hat{x} and \hat{p} with the ladder operators,

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}} (\hat{a} + \hat{a}^\dagger), \quad \hat{p} = \frac{1}{i} \sqrt{\frac{m\hbar\omega}{2}} (\hat{a} - \hat{a}^\dagger), \quad (9.28)$$

i.e.:

$$\langle \varphi_n | \hat{V} | \varphi_m \rangle = -F \sqrt{\frac{\hbar}{2m\omega}} \langle \varphi_n | \hat{a} + \hat{a}^\dagger | \varphi_m \rangle = -F \sqrt{\frac{\hbar}{2m\omega}} \left(\sqrt{n+1} \delta_{m,n+1} + \sqrt{n} \delta_{m,n-1} \right). \quad (9.29)$$

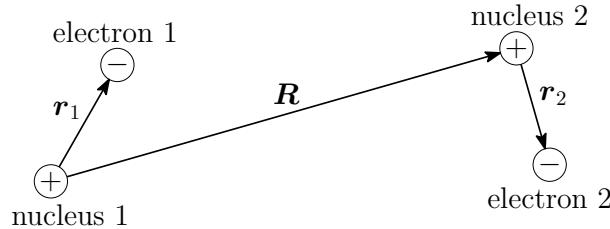


Figure 9.1: Two hydrogen atoms.

It follows that $E_n^{(1)} = \langle \varphi_n | \hat{V} | \varphi_n \rangle = 0$ for the first order. The second order gives

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \varphi_n | \hat{V} | \varphi_m \rangle|^2}{\varepsilon_n - \varepsilon_m} = \frac{|\langle \varphi_n | \hat{V} | \varphi_{n+1} \rangle|^2}{-\hbar\omega} + \frac{|\langle \varphi_n | \hat{V} | \varphi_{n-1} \rangle|^2}{\hbar\omega} = -\frac{F^2}{2m\omega^2}. \quad (9.30)$$

This already is the exact solution: all higher orders give no contribution. The correction of the state in first order is

$$\begin{aligned} |\phi_n^{(1)}\rangle &= \sum_{m \neq n} \frac{1}{\varepsilon_n - \varepsilon_m} |\varphi_m\rangle \langle \varphi_m | \hat{V} | \varphi_n \rangle \\ &= -F \sqrt{\frac{\hbar}{2m\omega}} \left(\frac{\sqrt{n+1}}{-\hbar\omega} |\varphi_{n+1}\rangle + \frac{\sqrt{n}}{\hbar\omega} |\varphi_{n-1}\rangle \right) \\ &= -\frac{iF}{m\hbar\omega^2} \sqrt{\frac{m\hbar\omega}{2}} \frac{1}{i} (\hat{a} - \hat{a}^\dagger) |\varphi_n\rangle \\ &= -\frac{iF}{m\hbar\omega^2} \hat{p} |\varphi_n\rangle, \end{aligned} \quad (9.31)$$

which corresponds to the first order in the expansion of the exact eigenstate $|\bar{\psi}_n\rangle$ in (9.27), i.e., for small F this is equivalent to a shift of the equilibrium point. The renormalization constant Z_n in second order in F is

$$\begin{aligned} Z_n &= 1 - \sum_{m \neq n} \frac{|\langle \varphi_n | \hat{V} | \varphi_m \rangle|^2}{(\varepsilon_n - \varepsilon_m)^2} \\ &= 1 - \left(\frac{|\langle \varphi_n | \hat{V} | \varphi_{n+1} \rangle|^2}{(-\hbar\omega)^2} + \frac{|\langle \varphi_n | \hat{V} | \varphi_{n-1} \rangle|^2}{(\hbar\omega)^2} \right) \\ &= 1 - \frac{F^2(2n+1)}{2m\hbar\omega^3}, \end{aligned} \quad (9.32)$$

in agreement with (9.23).

9.3 Applications of perturbation theory: Van-der-Waals interaction

We consider two hydrogen atoms (Fig. 9.1) whose nuclei have the distance vector \mathbf{R} . The internal coordinates for the position of the respective electron are denoted

by \mathbf{r}_1 and \mathbf{r}_2 , respectively. The Hamilton operator is

$$\hat{H} = \hat{H}_{0,1} + \hat{H}_{0,2} + \hat{V}, \quad (9.33)$$

where $\hat{H}_{0,i}$ are the Hamilton operators of the unperturbed atoms, with eigenstates $|\varphi_{i,n}\rangle$ and energy eigenvalues ε_n ($i = 1, 2$). The perturbation \hat{V} is the Coulomb interaction between the atoms:

$$\hat{V} = e^2 \left[\frac{1}{R} + \frac{1}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|} - \frac{1}{|\mathbf{R} + \mathbf{r}_2|} - \frac{1}{|\mathbf{R} - \mathbf{r}_1|} \right], \quad (9.34)$$

with $R = |\mathbf{R}|$. We assume that the two atoms are much farther apart than the Bohr radius, $R \gg a_0$. Then we can perform a Taylor expansion in powers of \mathbf{r}_1/R and \mathbf{r}_2/R . The first non-vanishing term is second order and has the following form:

$$\hat{V} \approx -e^2(\mathbf{r}_1 \cdot \nabla)(\mathbf{r}_2 \cdot \nabla) \frac{1}{R} = e^2 \left[\frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{R^3} - \frac{3(\mathbf{r}_1 \cdot \mathbf{R})(\mathbf{r}_2 \cdot \mathbf{R})}{R^5} \right]. \quad (9.35)$$

For the sake of simplicity we choose $\mathbf{R} \parallel z$, so that

$$\hat{V} = \frac{e^2}{R^3}(x_1 x_2 + y_1 y_2 - 2z_1 z_2). \quad (9.36)$$

We assume that both atoms are in their ground state, $|\varphi_{1,1}\rangle$ and $|\varphi_{2,1}\rangle$, i.e., their unperturbed energy is $2\varepsilon_1$. We can immediately write the correction for the energy, up to first order:

$$\begin{aligned} E(R) &= 2\varepsilon_1 + \langle \varphi_{1,1}, \varphi_{2,1} | \hat{V} | \varphi_{1,1}, \varphi_{2,1} \rangle \\ &= 2\varepsilon_1 + \frac{e^2}{R^3} (\langle \varphi_{1,1} | \hat{x}_1 | \varphi_{1,1} \rangle \langle \varphi_{2,1} | \hat{x}_2 | \varphi_{2,1} \rangle \\ &\quad + \langle \varphi_{1,1} | \hat{y}_1 | \varphi_{1,1} \rangle \langle \varphi_{2,1} | \hat{y}_2 | \varphi_{2,1} \rangle - 2\langle \varphi_{1,1} | \hat{z}_1 | \varphi_{1,1} \rangle \langle \varphi_{2,1} | \hat{z}_2 | \varphi_{2,1} \rangle). \end{aligned} \quad (9.37)$$

It is clear that the ground states of both atoms have angular momentum $l = 0$ while the operator $\hat{\mathbf{r}}_i$ is a vector operator. Therefore all matrix elements vanish in the first order correction, because of the selection rule (8.72) in Chapter 8.

The first non-vanishing correction therefore comes in second order:

$$E^{(2)}(R) = \frac{e^4}{R^6} \underbrace{\sum_{(n_1, n_2) \neq (1, 1)} \frac{|\langle \varphi_{1,1}, \varphi_{2,1} | (\hat{x}_1 \hat{x}_2 + \hat{y}_1 \hat{y}_2 - 2\hat{z}_1 \hat{z}_2) | \varphi_{1,n_1}, \varphi_{2,n_2} \rangle|^2}{2\varepsilon_1 - \varepsilon_{n_1} - \varepsilon_{n_2}}}_{= -\zeta a_0^5/e^2}, \quad (9.38)$$

where the sum runs over all quantum numbers which are different from those of the ground state. ζ is a dimensionless parameter which has to be calculated. For our case, $\zeta \approx 6.5$ is obtained. Thus the energy correction is

$$E(R) = 2\varepsilon_1 - \frac{e^2}{a_0} \left(\frac{a_0}{R} \right)^6 \zeta, \quad (9.39)$$

i.e., we find an effective attractive potential between the two hydrogen atoms, which decreases over long distances with R^{-6} . This is the *Van-der-Waals interaction* between neutral atoms. The picture behind this interaction is that the atoms polarize each other and thus can lower the energy. This simple perturbation theory is no longer sufficient, when R becomes of a size similar to the Bohr radius a_0 . For closer distances there is a repulsive interaction because of the repulsion of the electrons and the Pauli principle. Furthermore, as we will see in Quantum Mechanics II, the covalent bond between the two atoms comes also into play.

9.4 Perturbation theory for degenerate states

In the case of degenerate eigenstates of \hat{H}_0 the difficulty arises, that the energy denominators, which occur in expressions like $\langle \varphi_n | \hat{V} | \varphi_m \rangle / (\varepsilon_n - \varepsilon_m)$, vanish. This is a problem, as soon as the matrix element $\langle \varphi_n | \hat{V} | \varphi_m \rangle \neq 0$. Then the simple power series expansion is not possible.

We consider now the N degenerate states $|\varphi_{n_1}\rangle, |\varphi_{n_2}\rangle, \dots, |\varphi_{n_N}\rangle$ with the energy eigenvalue ε_n . In order to successfully carry out the perturbative expansion, we need to find a unitary transformation,

$$|\varphi'_{n_\alpha}\rangle = \sum_{i=1}^N u_{\alpha,i} |\varphi_{n_i}\rangle, \quad (9.40)$$

so that the matrix elements are $\langle \varphi'_{n_\alpha} | \hat{V} | \varphi'_{n_\beta} \rangle = 0$ for $\alpha \neq \beta$. This means that we have to diagonalize the matrix $\langle \varphi_{n_i} | \hat{V} | \varphi_{n_j} \rangle = V_{ij}^{(1)}$, corresponding to the eigenvalue problem

$$\sum_{j=1}^N V_{ij}^{(1)} u_{\alpha,j} = E_{n_\alpha}^{(1)} u_{\alpha,i}, \quad (9.41)$$

i.e., according to (9.40) the rows of the matrix $u_{\alpha,i}$ are the eigenvectors of the matrix $V_{ij}^{(1)}$, with eigenvalues $E_{n_\alpha}^{(1)}$. Since \hat{V} is hermitian, the transformation matrix $u_{\alpha,i}$ is unitary if one demands $\sum_i |u_{\alpha,i}|^2 = 1$, i.e., the new basis is also orthonormal.

The matrix elements of \hat{V} in the new basis $|\varphi'_{n_\alpha}\rangle$ are

$$\langle \varphi'_{n_\alpha} | \hat{V} | \varphi'_{n_\beta} \rangle = E_{n_\alpha}^{(1)} \delta_{\alpha,\beta} \quad (9.42)$$

and correspond to the energy corrections in first order perturbation theory. Using the new basis for the degenerate states we can now continue the perturbative expansion without problems, with the sums running over all non-degenerate states:

$$|\psi_{n_\alpha}\rangle = |\varphi'_{n_\alpha}\rangle + \lambda \sum_{m \neq n_1, \dots, n_N} |\varphi_m\rangle \frac{\langle \varphi_m | \hat{V} | \varphi'_{n_\alpha} \rangle}{\varepsilon_n - \varepsilon_m} + \dots \quad (9.43)$$

for the state and

$$E_{n_\alpha} = \varepsilon_n + \lambda \langle \varphi'_{n_\alpha} | \hat{V} | \varphi'_{n_\alpha} \rangle + \lambda^2 \sum_{m \neq n_1, \dots, n_N} \frac{|\langle \varphi_m | \hat{V} | \varphi'_{n_\alpha} \rangle|^2}{\varepsilon_n - \varepsilon_m} + \dots \quad (9.44)$$

for the energy.

There are cases in which $\langle \varphi_{n_i} | \hat{V} | \varphi_{n_j} \rangle = 0$ for all i, j . Then we can go to the second order. But caution is required, because of the energy denominators: the second-order matrix to be diagonalized has the form

$$V_{ij}^{(2)} = \sum_{m \neq n_1, \dots, n_N} \frac{\langle \varphi_{n_i} | \hat{V} | \varphi_m \rangle \langle \varphi_m | \hat{V} | \varphi_{n_j} \rangle}{\varepsilon_n - \varepsilon_m}, \quad (9.45)$$

where the sum excludes all m which belong to the set of degenerate states with energy ε_n . This saves us from vanishing energy denominators in third order perturbation theory. This matrix is also Hermitian and leads to a unitary transformation analogous to the first order case. If necessary, this can be continued to arbitrary higher orders.

As we have seen, the degeneracy and the resulting vanishing of the energy denominators cause difficulties for the perturbative expansion. Problems arise, however, already when $|\langle \varphi_n | \hat{V} | \varphi_m \rangle| \gg |\varepsilon_n - \varepsilon_m|$, because then the corrections are large. We call this situation *almost degenerate*, i.e., the energies of two or more states are close to each other. Here it is also necessary to follow a procedure as in the degenerate case, before the conventional perturbative expansion is started.

9.5 Applications of perturbation theory: the Stark effect

Given is a hydrogen atom in a weak electric field. We consider the states with quantum number $n = 2$, which are four-fold degenerate. We have in fact seen that the states

$$|n, l, m\rangle = |2, 0, 0\rangle, |2, 1, +1\rangle, |2, 1, 0\rangle, |2, 1, -1\rangle \quad (9.46)$$

are degenerate with energy $E_2 = -e^2/8a_0$. The Hamilton operator \hat{H}_0 corresponds to the unperturbed hydrogen atom, and the electric field enter in \hat{V} ,

$$\hat{V} = -(-e)E_z \hat{z} = eE_z \sqrt{\frac{4\pi}{3}} r Y_{1,0}(\theta, \phi), \quad (9.47)$$

where we have assumed without restriction of generality that the electric field is parallel to the z -axis and we represent z in spherical coordinates. Now we can calculate the matrix elements between the degenerate states. To do this we can use the selection rules from chapter 8, since \hat{V} is a tensor operator with $(k, q) = (1, 0)$. From (8.65) and (8.72) follows, that $\langle 2, l', m' | \hat{V} | 2, l'', m'' \rangle$ is different from zero only if $|l' - l''| = 1$ and $m' = m''$. This is satisfied only by the matrix elements $\langle 2, 0, 0 | \hat{V} | 2, 1, 0 \rangle$ and $\langle 2, 1, 0 | \hat{V} | 2, 0, 0 \rangle$. From a concrete computation one finds:

$$\langle 2, 0, 0 | \hat{V} | 2, 1, 0 \rangle = \langle 2, 1, 0 | \hat{V} | 2, 0, 0 \rangle = -3a_0 e E_z. \quad (9.48)$$

Thus, for these two states we get the matrix

$$\begin{pmatrix} 0 & -3a_0 e E_z \\ -3a_0 e E_z & 0 \end{pmatrix}. \quad (9.49)$$

Its diagonalization gives the two new states,

$$|\phi_{\pm}\rangle = \frac{1}{\sqrt{2}} (|2, 0, 0\rangle \pm |2, 1, 0\rangle) \quad (9.50)$$

with the energies (in first order)

$$E_{\pm} = -\frac{e^2}{8a_0} \mp 3a_0 e E_z. \quad (9.51)$$

This means that if the atom was originally in the state $|2, 0, 0\rangle$, the electric field causes an admixture of a p -wave state ($l = 1$). Despite the diagonalization, the two states $|2, 1, \pm 1\rangle$ still remain degenerate. This degeneracy is only removed by the second order corrections.

9.6 Applications of perturbation theory: Zeeman effect and spin-orbit coupling

We can now continue the study of a hydrogen atom in an external magnetic field $\mathbf{B} = (0, 0, B_z)$ by also considering the spin degrees of freedom. The Hamilton operator is

$$\hat{H} = \underbrace{\frac{\hat{\mathbf{p}}^2}{2m_e}}_{\hat{H}_0} + V(\hat{r}) + \underbrace{\frac{eB_z}{2m_ec}(\hat{L}_z + 2\hat{S}_z)}_{\hat{H}_Z} + \underbrace{\frac{1}{2m_e^2c^2}\frac{1}{\hat{r}}\frac{dV}{dr}\hat{\mathbf{S}} \cdot \hat{\mathbf{L}}}_{\hat{H}_{SB}}, \quad (9.52)$$

with the Coulomb potential $V(\hat{r}) = -e^2/\hat{r}$. The three terms are: \hat{H}_0 the Hamilton operator of the unperturbed hydrogen atom, \hat{H}_Z the Zeeman term and \hat{H}_{SB} the spin-orbit coupling¹.

We can choose between two sets of basis states. On the one side the operators \hat{H}_0 , $\hat{\mathbf{L}}^2$, \hat{L}_z , $\hat{\mathbf{S}}^2$ and \hat{S}_z commute and we can use their common eigenstates $|n, l, m_l, s, m_s\rangle$. On the other side, if we define the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, the operators \hat{H}_0 , $\hat{\mathbf{L}}^2$, $\hat{\mathbf{S}}^2$, $\hat{\mathbf{J}}^2$ and \hat{J}_z commutes and we can define the common eigenstates $|n, l, s, j, m_j\rangle$. We will see that the choice of the suitable basis depends on the strength of the external magnetic field.

why

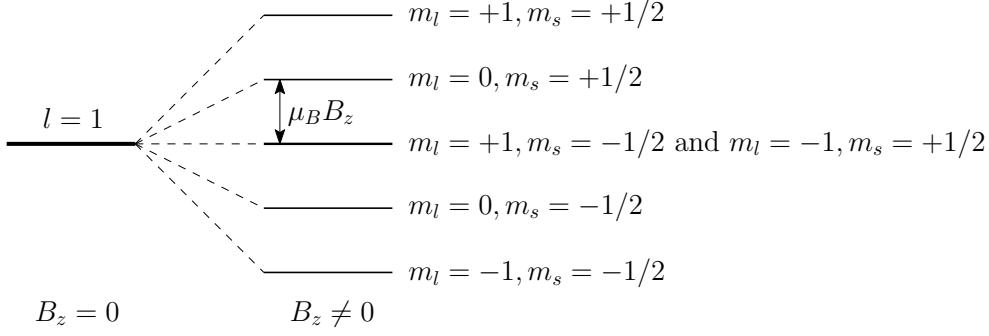
For large magnetic fields, \hat{H}_Z is dominant over \hat{H}_{SB} and we can neglect the latter term. Because of $\hat{H}_Z \propto \hat{L}_z + 2\hat{S}_z$ the basis states $|n, l, m_l, s, m_s\rangle$ are also eigenstates of \hat{H}_Z :

$$\hat{H}_Z|n, l, m_l, s, m_s\rangle = \frac{e\hbar B_z}{2m_e c} (m_l + 2m_s)|n, l, m_l, s, m_s\rangle. \quad (9.53)$$

The energy eigenvalues of the electron are thus

$$E = -\frac{Ry}{n^2} + \frac{e\hbar B_z}{2m_e c} (m_l + 2m_s), \quad (9.54)$$

¹Further correction terms will be treated in Quantum Mechanics II: here we neglect them.


 Figure 9.2: Splitting of the $l = 1$ -states in a strong magnetic field.

and depends on $m_l = -l, \dots, l$ and $m_s = \pm 1/2$: the degeneracy is partially lifted. We consider as example the states with $l = 1$: without magnetic field they are 6-fold degenerate, since m_l (m_s) can take three (two) values. Figure 9.2 shows the splitting of the energy degeneracy in a strong magnetic field: since the gyromagnetic factor of the electron $g_e \approx 2$, two states remain degenerate and we get a quintuplet.

For small magnetic fields \hat{H}_{SB} is dominant and at first we neglect \hat{H}_Z . The states $|n, l, m_l, s, m_s\rangle$ are no more a suitable basis, since the product $\hat{\mathbf{S}} \cdot \hat{\mathbf{L}}$ is invariant only under a simultaneous rotation of $\hat{\mathbf{S}}$ and $\hat{\mathbf{L}}$ and thus \hat{H}_{SB} is not diagonal in this basis. Here we use the eigenstates $|n, l, s, j, m_j\rangle$ of the total angular momentum $\hat{\mathbf{J}}$. In fact

$$\hat{\mathbf{S}} \cdot \hat{\mathbf{L}} = \frac{1}{2} \left((\hat{\mathbf{L}} + \hat{\mathbf{S}})^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2 \right) \quad (9.55)$$

holds and therefore the eigenvalue equation

$$\hat{\mathbf{S}} \cdot \hat{\mathbf{L}} |n, l, s, j, m_j\rangle = \frac{\hbar^2}{2} (j(j+1) - l(l+1) - s(s+1)) |n, l, s, j, m_j\rangle \quad (9.56)$$

follows. Notice that for $l = 0$ we have $j = s$, i.e., the eigenvalue is 0 and there is no spin-orbit coupling; we continue our discussion for $l \neq 0$. Taking into account

$$\frac{1}{r} \frac{dV}{dr} = \frac{e^2}{r^3} \quad (9.57)$$

and $s = 1/2$, $j = l \pm 1/2$, we get the (first order) perturbative energy correction for the spin-orbit coupling:

$$\begin{aligned} \Delta E_{SB} &= \langle n, l, s, j, m_j | \hat{H}_{SB} | n, l, s, j, m_j \rangle \\ &= \frac{e^2 \hbar^2}{4m_e^2 c^2} \langle n, l | \frac{1}{r^3} | n, l \rangle \begin{cases} l, & \text{for } j = l + \frac{1}{2} \\ -(l+1), & \text{for } j = l - \frac{1}{2} \end{cases}. \end{aligned} \quad (9.58)$$

With the expectation value

$$\langle n, l | \frac{1}{r^3} | n, l \rangle = \frac{1}{a_0^3 n^3} \frac{1}{l(l+\frac{1}{2})(l+1)} \quad (9.59)$$

we get the energy splitting

$$\Delta E_{SB} = \frac{\alpha^2 \text{Ry}}{2n^3} \frac{1}{l(l+\frac{1}{2})(l+1)} \begin{cases} l, & \text{for } j = l + \frac{1}{2} \\ -(l+1), & \text{for } j = l - \frac{1}{2} \end{cases}, \quad (9.60)$$

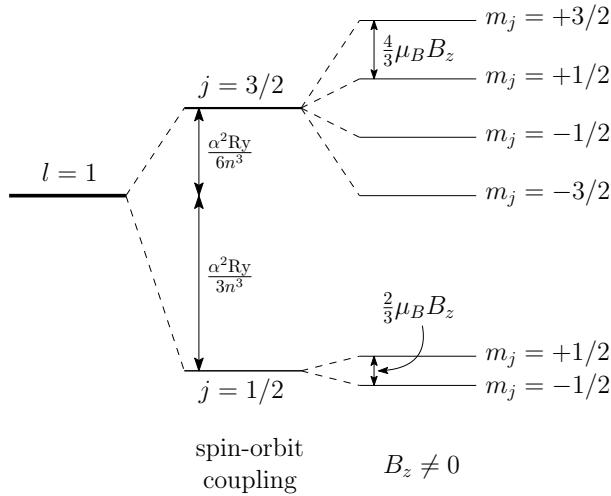


Figure 9.3: Splitting of the $l = 1$ -states in a weak magnetic field.

where $\alpha = e^2/\hbar c = 1/137$ is the fine structure constant, $a_0 = \hbar^2/m_e e^2$ the Bohr's radius and $\text{Ry} = e^2/2a_0$ the Rydberg constant.

Now we can also determine the first order perturbative correction of the Zeeman term for a weak magnetic field, by computing the expectation value

$$\Delta E_Z = \langle n, l, s, j, m_j | \hat{H}_Z | n, l, s, j, m_j \rangle. \quad (9.61)$$

The Zeeman term is, with $\mathbf{J} = \mathbf{L} + \mathbf{S}$,

$$\hat{H}_Z = \frac{eB_z}{2m_e c} (\hat{L}_z + 2\hat{S}_z) = \frac{eB_z}{2m_e c} (\hat{J}_z + \hat{S}_z). \quad (9.62)$$

The expectation value of \hat{J}_z is simply $\hbar m_j$. We still need the expectation value of \hat{S}_z . For this purpose we can use equation (8.64):

$$\langle n, l, s, j, m_j | \hat{S}_z | n, l, s, j, m_j \rangle = \frac{\langle n, l, s, j | \hat{S} \cdot \hat{J} | n, l, s, j \rangle}{\hbar^2 j(j+1)} \langle n, l, s, j, m_j | \hat{J}_z | n, l, s, j, m_j \rangle. \quad (9.63)$$

With the relation

$$\hat{S} \cdot \hat{J} = -\frac{1}{2} \left(\underbrace{(\hat{J} - \hat{S})^2}_{\hat{L}^2} - \hat{J}^2 - \hat{S}^2 \right) \quad (9.64)$$

we get

$$\langle n, l, s, j, m_j | \hat{S}_z | n, l, s, j, m_j \rangle = \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \hbar m_j \quad (9.65)$$

and from it the energy correction

$$\Delta E_Z = \frac{e\hbar B_z}{2m_e c} m_j \left(1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right), \quad (9.66)$$

with $m_j = -j, \dots, j$. The $2j + 1$ degeneracy of the states, which was still present in the splitting generated by the spin-orbit coupling (9.60), is now lifted. We consider again as an example the $l = 1$ -states: without spin-orbit coupling and magnetic field, they are 6-fold degenerate. The spin-orbit coupling separates the $j = 1/2$ (2-fold degenerate) from the $j = 3/2$ (4-fold degenerate) states. The external magnetic field completely lifts the degeneracy, as shown in figure 9.3.

9.7 Brillouin-Wigner perturbation theory

An approach to perturbation theory which allows a simpler access to the higher order corrections than in the Rayleigh-Schrödinger formulation is due to Brillouin and Wigner. Essentially, the starting point is the same,

$$(E_n - \hat{H}_0)|\psi_n\rangle = \lambda \hat{V}|\psi_n\rangle. \quad (9.67)$$

Again, we assume $\langle \varphi_n | \psi_n \rangle = 1$ for the exact state $|\psi_n\rangle$ we wish to determine by the perturbative expansion, i.e., $|\psi_n\rangle$ is at first not normalized. We multiply now (9.67) with $\langle \varphi_m |$ and (with $\langle \varphi_m | \hat{H}_0 | \psi_m \rangle = \varepsilon_m \langle \varphi_m | \psi_m \rangle$) we get

$$\langle \varphi_m | \psi_n \rangle = \lambda \frac{\langle \varphi_m | \hat{V} | \psi_n \rangle}{E_n - \varepsilon_m}, \quad (9.68)$$

where, remark, E_n is the exact energy and $|\psi_n\rangle$ the exact eigenstate of \hat{H} . Thus we can now express $|\psi_n\rangle$ as

$$|\psi_n\rangle = |\varphi_n\rangle + \lambda \sum_{m \neq n} |\varphi_m\rangle \frac{1}{E_n - \varepsilon_m} \langle \varphi_m | \hat{V} | \psi_n \rangle. \quad (9.69)$$

From this we can derive a series for $|\psi_n\rangle$ by iteratively inserting the right hand side:

$$\begin{aligned} |\psi_n\rangle &= |\varphi_n\rangle + \lambda \sum_{m \neq n} |\varphi_m\rangle \frac{1}{E_n - \varepsilon_m} \langle \varphi_m | \hat{V} | \varphi_n \rangle \\ &\quad + \lambda^2 \sum_{k, m \neq n} |\varphi_k\rangle \frac{1}{E_n - \varepsilon_k} \langle \varphi_k | \hat{V} | \varphi_m \rangle \frac{1}{E_n - \varepsilon_m} \langle \varphi_m | \hat{V} | \varphi_n \rangle + \dots \end{aligned} \quad (9.70)$$

This expansion is implicit, in the sense that in the denominators on the right hand side stands the (unknown) exact energy. If we expand E_n as well, then we would again generate the Rayleigh-Schrödinger version of perturbation theory. With a good estimate for E_n , this series can converge faster than the Rayleigh-Schrödinger series. Furthermore, we can use $|\psi_n\rangle$ from (9.70) to express E_n up to a certain order. This results in an implicit nonlinear equation for E_n , e.g. from

$$\langle \varphi_n | E_n - \hat{H}_0 | \psi_n \rangle = \lambda \langle \varphi_n | \hat{V} | \psi_n \rangle \quad (9.71)$$

follows, in second order,

$$E_n = \varepsilon_n + \lambda \langle \varphi_n | \hat{V} | \varphi_n \rangle + \lambda^2 \sum_{m \neq n} \frac{|\langle \varphi_m | \hat{V} | \varphi_n \rangle|^2}{E_n - \varepsilon_m} + \dots, \quad (9.72)$$

which can be solved numerically. The advantage of the Brillouin-Wigner perturbation theory is the formal simplicity to arbitrary order; its disadvantage is the implicit form.

9.8 Variational approximation of the ground state

In many cases we are only interested in a good approximation for the ground state of the system. For this purpose there is a method which is based on the Rayleigh-Ritz variational principle and can even be applied to problems for which the perturbative approach is not suitable.

We consider the Hamilton operator \hat{H} , which we could write in the spectral representation,

$$\hat{H} = \sum_n E_n |\psi_n\rangle\langle\psi_n|, \quad (9.73)$$

if we could solve it exactly. Let the states be ordered, so that $E_0 \leq E_1 \leq E_2 \leq \dots$. We take an arbitrary state $|\phi\rangle$ and calculate the expectation value $\langle\phi|\hat{H}|\phi\rangle$. We get:

$$\langle\phi|\hat{H}|\phi\rangle = \sum_n E_n \langle\phi|\psi_n\rangle\langle\psi_n|\phi\rangle \geq E_0 \sum_n \langle\phi|\psi_n\rangle\langle\psi_n|\phi\rangle = E_0 \langle\phi|\phi\rangle, \quad (9.74)$$

since $\{|\psi_n\rangle\}$ is an orthonormal basis. Consequently, it results

$$\frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} \geq E_0, \quad (9.75)$$

an upper bound for the ground state energy. This bound is of course only as good as our ability to choose the state $|\phi\rangle$ close to the ground state $|\psi_0\rangle$, i.e., the squared scalar product $|\langle\phi|\psi_0\rangle|^2/\langle\phi|\phi\rangle$ should be as close to 1 as possible. Notice that we can optimize the state if it has free parameters, by minimizing the variational energy according to these parameters.

We want to illustrate this idea with the example of the helium atom. The helium atom with two electrons is, unlike the hydrogen atom, not exactly solvable. The difficulty lies in the mutual repulsion of the two electrons. The Hamilton operator has the form

$$\hat{H} = \frac{1}{2m} (\hat{\mathbf{p}}_1^2 + \hat{\mathbf{p}}_2^2) - e^2 \left(\frac{2}{\hat{r}_1} + \frac{2}{\hat{r}_2} - \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} \right), \quad (9.76)$$

where the indices 1 and 2 of the operators designate the two electrons. We now set a variational wave function for the ground state in the form of a product state. Here we are guided by the ground state wave function of the electron in the hydrogen atom:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_1)f(\mathbf{r}_2) \quad \text{with} \quad f(\mathbf{r}) = \sqrt{\frac{\kappa^3}{\pi}} e^{-\kappa r}, \quad (9.77)$$

where $\kappa > 0$ and the wave function is normalized²

²We can put both electrons into the same state, if we assume that they have different spin states. This means that the total spin of the electrons vanishes: a spin singlet state.

We compute now the expectation value of the energy $E = \langle \hat{H} \rangle$ in this state. From $\int_{\mathbb{R}^3} d^3r f(\nabla^2 f) = - \int_{\mathbb{R}^3} d^3r |\nabla f|^2$ for functions which vanish at infinity, we get the kinetic energy of the first electron:

$$\begin{aligned}
 \langle \frac{\hat{\mathbf{p}}_1^2}{2m} \rangle &= -\frac{\hbar^2}{2m} \int_{\mathbb{R}^3} d^3r_1 \int_{\mathbb{R}^3} d^3r_2 f(\mathbf{r}_1) f(\mathbf{r}_2) \nabla_1^2 f(\mathbf{r}_1) f(\mathbf{r}_2) \\
 &= \frac{\hbar^2}{2m} \int_{\mathbb{R}^3} d^3r_1 |\nabla f(\mathbf{r}_1)|^2 \underbrace{\int_{\mathbb{R}^3} d^3r_2 |f(\mathbf{r}_2)|^2}_1 \\
 &= \frac{\hbar^2}{2m} \int_0^\infty dr_1 4\pi r_1^2 \underbrace{\left| \frac{\partial f(r_1)}{\partial r_1} \right|^2}_{|-\kappa f(r_1)|^2} \\
 &= \frac{\hbar^2 \kappa^2}{2m} \int_0^\infty dr_1 4\pi r_1^2 |f(r_1)|^2 \\
 &= \frac{\hbar^2 \kappa^2}{2m}
 \end{aligned} \tag{9.78}$$

and analogously $\langle \hat{\mathbf{p}}_2^2/2m \rangle = \hbar^2 \kappa^2/2m$. For the potential energy of the first electron in the electric field of the nucleus we get

$$\begin{aligned}
 \langle -\frac{2e^2}{\hat{r}_1} \rangle &= -2e^2 \int_{\mathbb{R}^3} d^3r_1 \frac{1}{r_1} |f(\mathbf{r}_1)|^2 \underbrace{\int_{\mathbb{R}^3} d^3r_2 |f(\mathbf{r}_2)|^2}_1 \\
 &= -8\pi e^2 \int_0^\infty dr_1 \frac{\kappa^3}{\pi} \underbrace{r_1 e^{-2\kappa r_1}}_{-\frac{1}{2} \frac{\partial}{\partial \kappa} e^{-2\kappa r_1}} \\
 &= 4e^2 \kappa^3 \frac{\partial}{\partial \kappa} \underbrace{\int_0^\infty dr_1 e^{-2\kappa r_1}}_{\frac{1}{2\kappa}} \\
 &= -2e^2 \kappa
 \end{aligned} \tag{9.79}$$

and analogously $\langle -2e^2/\hat{r}_2 \rangle = -2e^2 \kappa$. Finally, because of the symmetry $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$, we

can write the interaction energy of the two electrons as

$$\begin{aligned}
 \langle \frac{e^2}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} \rangle &= 2e^2 \int d^3 r_1 |f(\mathbf{r}_1)|^2 \int_{r_2 \leq r_1} d^3 r_2 \frac{|f(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \\
 &= 2e^2 \int d^3 r_1 |f(\mathbf{r}_1)|^2 \int_0^{r_1} dr_2 r_2^2 |f(r_2)|^2 \times \\
 &\quad \underbrace{\int_0^{2\pi} d\phi \int_{-1}^1 d\cos\theta}_{2\pi} \underbrace{\frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}}}_{\frac{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}}{-r_1 r_2} \Big|_{-1}^1 = \frac{|r_1 - r_2| - (r_1 + r_2)}{-r_1 r_2} = \frac{2}{r_1}} \\
 &= 32\pi^2 e^2 \int_0^\infty dr_1 r_1 |f(r_1)|^2 \underbrace{\int_0^{r_1} dr_2 r_2^2 |f(r_2)|^2}_{\frac{1}{4} \frac{\kappa^3}{\pi} \frac{\partial^2}{\partial \kappa^2} \int_0^{r_1} dr_2 e^{-2\kappa r_2}} \\
 &= 8\pi e^2 \kappa^3 \int_0^\infty dr_1 r_1 |f(r_1)|^2 \underbrace{\frac{\partial^2}{\partial \kappa^2} \left(\frac{1 - e^{-2\kappa r_1}}{2\kappa} \right)}_{\frac{e^{-2\kappa r_1}(-1 - 2\kappa r_1 - 2\kappa^2 r_1^2) + 1}{\kappa^3}} \\
 &= 8\pi e^2 \frac{\kappa^3}{\pi} \int_0^\infty dr_1 (-r_1 - 2\kappa r_1^2 - 2\kappa^2 r_1^3) e^{-4\kappa r_1} + r_1 e^{-2\kappa r_1} \\
 &\quad \underbrace{\left(\frac{1}{4} \frac{\partial}{\partial \kappa} - \frac{\kappa}{8} \frac{\partial^2}{\partial \kappa^2} + \frac{\kappa^2}{32} \frac{\partial^3}{\partial \kappa^3} \right) \frac{1}{4\kappa} - \frac{1}{2} \frac{\partial}{\partial \kappa} \frac{1}{2\kappa} = \frac{5}{64\kappa^2}} \\
 &= \frac{5}{8} \kappa e^2. \tag{9.80}
 \end{aligned}$$

We define the dimensionless parameter $\beta = \kappa a_0$ with the Bohr's radius $a_0 = \hbar^2/m e^2$. The variational energy is then

$$E(\beta) = 2\text{Ry} \left(\beta^2 - 4\beta + \frac{5}{8}\beta \right) = 2\text{Ry} \left(\beta^2 - \frac{27}{8}\beta \right), \tag{9.81}$$

with the Rydberg constant $\text{Ry} = e^2/2a_0$. We can now minimize the energy with respect to β , in order to optimize the variational wave function. The minimization gives $\beta_{\min} = 27/16$ and the approximated ground state energy

$$E_{\min} = -2\text{Ry} \left(\frac{27}{16} \right)^2 = -5.695 \text{ Ry}. \tag{9.82}$$

The experimentally determined ground state energy (from ionization experiments) is $E = -5.807 \text{ Ry}$. We see that although we have obtained an upper bound, the discrepancy is relatively large. This is mainly because our product wave function does not take into account the mutual correlation of the two electrons. The interaction term gives for the above (*s*-wave symmetric) product wave function only a modification of the central Coulomb potential, i.e., the charge density of one electron partially shields the nuclear potential for the other electron. Taking into account the quantum numbers (and symmetries), also variational estimations for excited

states are possible, by restricting the variational wave functions in a certain Hilbert subspace which is defined by symmetries, e.g. by the angular momentum quantum numbers.

9.9 The WKB method: quasiclassical approximation

In this section we want to look at states with high energy, so that the wave length of the particle is short compared to the length scale over which the amplitude of the particle varies. We write the wave function in the following form:

$$\psi(x, t) = e^{\frac{i}{\hbar} S(x, t)}, \quad (9.83)$$

where we restrict the discussion to one-dimensional problems. We now expand $S(x, t)$ in powers of \hbar , with the meaning that for $\hbar \rightarrow 0$ the classical mechanics is restored.

The classical limit is understood in the following way. In the Hamilton-Jacobi formulation of classical mechanics we introduce the action function $S(x, p, t)$ with the property:

$$H(x, p, t) = H\left(x, \frac{\partial S}{\partial x}, t\right) = -\frac{\partial S}{\partial t}, \quad (9.84)$$

where for the momentum $p = \partial S / \partial x$ holds. For the Hamilton function $H = \frac{p^2}{2m} + V(x)$ we get then the following equation:

$$-\frac{\partial S}{\partial t} = \frac{1}{2m} \left(\frac{\partial S}{\partial x}\right)^2 + V(x). \quad (9.85)$$

We consider now the corresponding Schrödinger equation,

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi. \quad (9.86)$$

We insert the wave function $\psi(x, t) = e^{iS(x, t)/\hbar}$ and get:

$$-\frac{\partial S}{\partial t} = \frac{1}{2m} \left(\frac{\partial S}{\partial x}\right)^2 + V(x) - \frac{i\hbar}{2m} \frac{\partial^2 S}{\partial x^2}. \quad (9.87)$$

In the limiting case $\hbar \rightarrow 0$ this equation for $S(x, t)$ corresponds formally to the equation for the action function in the classical problem (9.85).

We now consider stationary problems, looking for solutions of the time-independent Schrödinger equation of the form $\psi(x) = e^{iS(x)/\hbar}$. Here we will only consider the first two terms in the expansion of $S(x)$:

$$S(x) = S_0(x) + i\hbar S_1(x) + \dots \quad (9.88)$$

If we now insert it in the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi = (E - V(x))\psi(x) \quad (9.89)$$

and sort the obtained equation with respect to the order of \hbar , then we get

$$\hbar^0 : \quad \left(\frac{\partial S_0}{\partial x} \right)^2 - 2m(E - V(x)) = 0, \quad (9.90)$$

$$\hbar^1 : \quad 2 \frac{\partial S_0}{\partial x} \frac{\partial S_1}{\partial x} - \frac{\partial^2 S_0}{\partial x^2} = 0. \quad (9.91)$$

The solution of the first equation gives

$$S_0(x) = \pm \int_{x_0}^x dx' \sqrt{2m(E - V(x'))} = \pm \int_{x_0}^x dx' p(x'), \quad (9.92)$$

where x_0 is the initial position of the particle and

$$p(x) = \sqrt{2m(E - V(x))}. \quad (9.93)$$

Notice that for periodic trajectories S_0 is the action variable, if we consider one rotation. This gives a connection with the Bohr-Sommerfeld quantization.

The second equation (9.91) can be rewritten as

$$2 \frac{\partial S_1}{\partial x} = \frac{\partial}{\partial x} \left(\ln \left| \frac{\partial S_0}{\partial x} \right| \right), \quad (9.94)$$

from which it follows:

$$S_1(x) = \frac{1}{2} \ln \left(\sqrt{2m(E - V(x))} \right) + \text{const} = \ln \sqrt{p(x)} + \text{const}. \quad (9.95)$$

This means that the wave function can be expressed with the following approximation:

$$\psi(x) \approx e^{\frac{i}{\hbar}(S_0 + i\hbar S_1)} = \frac{C}{\sqrt{p(x)}} e^{\pm \frac{i}{\hbar} \int_{x_0}^x dx' p(x')}. \quad (9.96)$$

This is the WKB approximation (due to Wentzel, Kramers and Brillouin). This approximation is justified if $\hbar S_1(x) \ll S_0(x)$, or equivalently, because of (9.91):

$$\hbar \frac{\partial^2 S_0}{\partial x^2} = 2\hbar \frac{\partial S_0}{\partial x} \frac{\partial S_1}{\partial x} \ll \left(\frac{\partial S_0}{\partial x} \right)^2. \quad (9.97)$$

This condition can be written in the form

$$\frac{\partial p(x)}{\partial x} \lambda(x) \ll p(x), \quad (9.98)$$

where the local de Broglie wave length is defined by $\lambda(x) = 2\pi\hbar/p(x)$. The interpretation is simple: the WKB approximation is valid as long as the wave length is much shorter than the characteristic spatial variation of the momentum (or $V(x)$). This is very similar to the condition of the eikonal approximation (in ray optics), where the wave length must be shorter than the characteristic length scale of the variations of the refractive index $n(x)$.

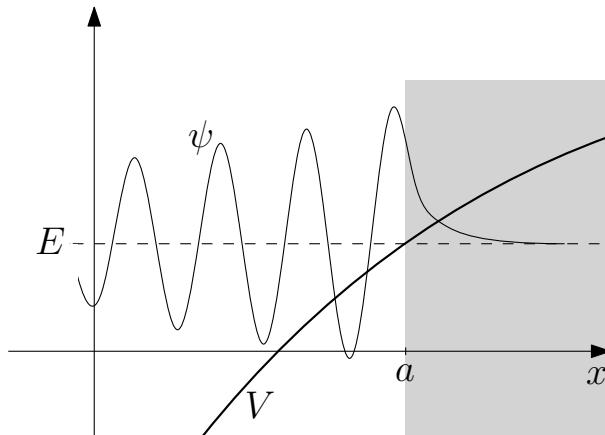


Figure 9.4: Potential and wave function in the proximity of a classical reversal point $x = a$.

The probability to find a particle in the interval $[x, x + dx]$ is

$$|\psi(x)|^2 dx = \frac{|C|^2}{p(x)} dx, \quad (9.99)$$

which is natural, since this probability should be inversely proportional to the local velocity. This proportionality holds because $dt = dx/v = mdx/p(x)$ corresponds to the time interval the particle needs to traverse the space interval.

We consider now the problem of the reversal points. It is clear that if along the trajectory of the particle we approach a point where $p(x)$ goes to zero, then the above criterion breaks down, and a more careful approach is necessary. We consider a particle in a potential as shown in figure (9.4).

In the classically allowed part of the phase space ($E > V(x)$, white region in Fig. 9.4) we have an incident and a reflected contribution to the wave function ψ . In the classical forbidden region ($E < V(x)$, gray region in Fig. 9.4), ψ decays exponentially. The behavior far from the classical reversal point a (with $E = V(a)$) is described by the WKB wave function. The analysis of how the two wavefunctions behave in the vicinity of the reversal point requires the solution of the complete Schrödinger equation. In the given case the potential $V(x)$ can be linearly approximated around $x = a$, and the solution of a particle in the linear potential is necessary. We will not go into the details of this calculation here³, and give only the result,

$$\psi(x) = \frac{C}{\sqrt{p(x)}} \sin \left(\frac{\pi}{4} + \frac{1}{\hbar} \int_x^a dx' p(x') \right) \quad (9.100)$$

for $x < a$ in the classically allowed region and

$$\psi(x) = \frac{C}{2\sqrt{|p(x)|}} \exp \left(-\frac{1}{\hbar} \int_a^x dx' |p(x')| \right) \quad (9.101)$$

³See for example Albert Messiah, *Quantum Mechanics*, Dover Publications.

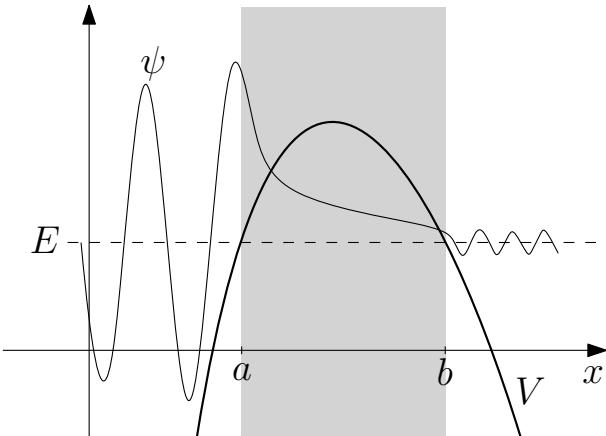


Figure 9.5: Tunneling through a potential barrier.

for $x > a$ in the classically forbidden region. Very important is the phase shift $\pi/4$ at the reversal point. This is universal for reversal points with linear potentials. For an infinitely hard reversal point (i.e., an infinitely high potential barrier) the phase shift is $\pi/2$.

If we now look at bound states in a potential well with two reversal points (left b and right a), then from the reversal point a we get the wave function (9.100) for $x < a$ and from the reversal point b for $x > b$ the wave function:

$$\psi(x) = \frac{C}{\sqrt{p(x)}} \sin \left(\frac{\pi}{4} + \frac{1}{\hbar} \int_b^x dx' p(x') \right). \quad (9.102)$$

In the allowed region $b < x < a$ both expressions (9.100) and (9.102) must be identical (up to a sign),

$$\begin{aligned} \sin \left(\frac{\pi}{4} + \frac{1}{\hbar} \int_b^x dx' p(x') \right) &= \sin \left(\frac{\pi}{4} + \frac{1}{\hbar} \int_b^a dx' p(x') - \frac{1}{\hbar} \int_x^a dx' p(x') \right) \\ &= -\sin \left(\frac{\pi}{4} + \frac{1}{\hbar} \int_x^a dx' p(x') - \left(\frac{1}{\hbar} \int_b^a dx' p(x') + \frac{\pi}{2} \right) \right) \\ &\stackrel{!}{=} \pm \sin \left(\frac{\pi}{4} + \frac{1}{\hbar} \int_x^a dx' p(x') \right), \end{aligned} \quad (9.103)$$

from which we get the condition

$$\frac{1}{\hbar} \int_b^a dx' p(x') + \frac{\pi}{2} = n\pi, \quad (9.104)$$

with n an integer. This corresponds to the Bohr-Sommerfeld quantization:

$$\frac{1}{2\pi} \oint p(x') dx' = \hbar \left(n + \frac{1}{2} \right), \quad (9.105)$$

from which we see that the unknown variable introduced in Chapter 1 is (in this case) $\alpha = 1/2$. Analogously, for hard reversal points we get $\alpha = 0$. Although the

quasiclassical approximation for small quantum numbers n is strictly speaking not applicable, it turns out that the quantization condition for many simple systems is nevertheless correct.

Another case for which the WKB method can be applied, is in the investigation of tunneling problems. Here we are mainly interested in the transmission probability of the particle through a potential barrier (Fig. 9.5). Without going into the details of the calculation, we give here the result:

$$|t(E)|^2 \approx \exp \left(-\frac{2}{\hbar} \int_a^b dx' \sqrt{2m(V(x') - E)} \right), \quad (9.106)$$

which also gives the exponential suppression of the transmission, as expected from our earlier discussions. The WKB method is particularly suitable for one-dimensional problems, where the classical path is clearly defined. This also includes orbits in a rotationally symmetric system. If this simplification does not apply, the WKB method can only be used if a clearly favored particle trajectory can be found. This holds specially for tunneling problems.

Chapter 10

Path integrals formulation of quantum mechanics

After the Schrödinger's representation of quantum mechanics with time-dependent states (wave mechanics) and the Heisenberg's representation with time-dependent operators (matrix mechanics), we now turn to a formulation of quantum mechanics, which concentrates on the propagator of particles. Let us consider a system with time-independent Hamilton operator \hat{H} . The time evolution of a state $|\psi\rangle$ from time t' to time t (with $t > t'$) is

$$|\psi(t)\rangle = \hat{U}(t, t')|\psi(t')\rangle. \quad (10.1)$$

Thereby, according to (3.106),

$$\hat{U}(t, t') = e^{-\frac{i}{\hbar}\hat{H}(t-t')} \quad (10.2)$$

is the time evolution operator.

We consider now the position representation by multiplying from the left with $\langle \mathbf{r}|$ and inserting an identity operator:

$$\underbrace{\langle \mathbf{r}|\psi(t)\rangle}_{\psi(\mathbf{r},t)} = \int d^3r' \langle \mathbf{r}|\hat{U}(t, t')|\mathbf{r}'\rangle \underbrace{\langle \mathbf{r}'|\psi(t')\rangle}_{\psi(\mathbf{r}',t')}. \quad (10.3)$$

If we compare this with the propagation of the wave function of a free particle (2.24) in chapter 2, we can define the propagator:

$$K(\mathbf{r}, \mathbf{r}'; t - t') = \langle \mathbf{r}|e^{-\frac{i}{\hbar}\hat{H}(t-t')}|\mathbf{r}'\rangle \Theta(t - t'). \quad (10.4)$$

The step function $\Theta(t - t')$ ensures that $t > t'$: we call this a *retarded propagator*.

We assume now to know the energy eigenvalues E_n and the corresponding eigenstates $|\phi_n\rangle$ of \hat{H} :

$$\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle. \quad (10.5)$$

Since these states form a complete orthonormal basis, i.e.,

$$1 = \sum_n |\phi_n\rangle\langle\phi_n|, \quad (10.6)$$

we can rewrite (10.4) as

$$K(\mathbf{r}, \mathbf{r}'; t - t') = \sum_n \langle \mathbf{r} | \phi_n \rangle e^{-\frac{i}{\hbar} E_n (t - t')} \langle \phi_n | \mathbf{r}' \rangle \Theta(t - t'). \quad (10.7)$$

Now we can perform a Fourier transform of $K(\mathbf{r}, \mathbf{r}'; t)$ with respect to time:

$$\begin{aligned} \tilde{K}(\mathbf{r}, \mathbf{r}'; E) &= \int_{-\infty}^{+\infty} dt e^{\frac{i}{\hbar}(E+i\eta)t} K(\mathbf{r}, \mathbf{r}'; t) \\ &= \sum_n \int_0^{\infty} dt e^{\frac{i}{\hbar}(E-E_n)t - \frac{\eta}{\hbar}t} \langle \mathbf{r} | \phi_n \rangle \langle \phi_n | \mathbf{r}' \rangle \\ &= i\hbar \sum_n \frac{\langle \mathbf{r} | \phi_n \rangle \langle \phi_n | \mathbf{r}' \rangle}{E - E_n + i\eta} \\ &= i\hbar \sum_n \frac{\phi_n(\mathbf{r}) \phi_n(\mathbf{r}')^*}{E - E_n + i\eta}, \end{aligned} \quad (10.8)$$

where $\phi_n(\mathbf{r}) = \langle \mathbf{r} | \phi_n \rangle$ is the wave function of the stationary state $|\phi_n\rangle$. We introduced the factor $e^{-\eta t/\hbar}$, with $\eta > 0$ and small, to ensure the convergence of the integral. We call $K(\mathbf{r}, \mathbf{r}'; t - t')$ (and its transform $\tilde{K}(\mathbf{r}, \mathbf{r}'; E)$) retarded Green's function of the quantum mechanical system. It contains all significant informations about the energy spectrum and particularly it describes the propagation of the wave function by given initial condition $\psi(\mathbf{r}, 0)$. We call (10.8) also spectral or Lehmann representation of the Green's function.

We now approach the propagator (10.4) from another side. We divide the time interval $[t', t]$ into N equal smaller intervals such that $t' = t_0$, $t = t_N$ and

$$t_j = t_0 + j \frac{t - t'}{N} = t_0 + j\epsilon, \quad j = 0, 1, \dots, N, \quad (10.9)$$

with $\epsilon = (t - t')/N$. We then rewrite (10.4) as

$$K(\mathbf{r}, \mathbf{r}'; t - t') = \langle \mathbf{r} | \prod_{j=1}^N e^{-\frac{i}{\hbar} \hat{H}(t_j - t_{j-1})} | \mathbf{r}' \rangle, \quad (10.10)$$

where we always assume $t > t'$ and neglect to write the Θ function. Inserting

$$1 = \int d^3 r_j |\mathbf{r}_j\rangle \langle \mathbf{r}_j|, \quad j = 1, \dots, N-1, \quad (10.11)$$

between all factors we get

$$\begin{aligned} K(\mathbf{r}, \mathbf{r}'; t - t') &= \int d^3 r_{N-1} d^3 r_{N-2} \cdots d^3 r_1 K(\mathbf{r}, \mathbf{r}_{N-1}; t_N - t_{N-1}) \times \\ &\quad \times K(\mathbf{r}_{N-1}, \mathbf{r}_{N-2}; t_{N-1} - t_{N-2}) \cdots K(\mathbf{r}_1, \mathbf{r}'; t_1 - t_0). \end{aligned} \quad (10.12)$$

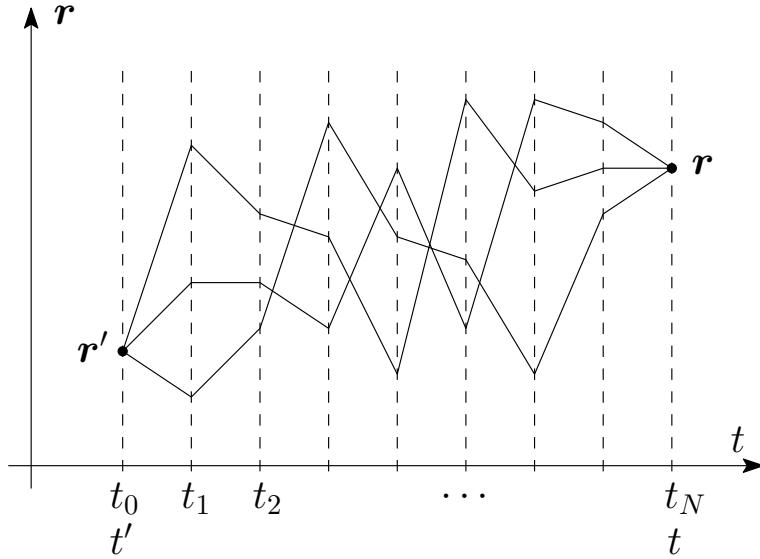


Figure 10.1: Discrete path from (\mathbf{r}', t') to (\mathbf{r}, t) .

If we hold the start and end points, \mathbf{r}' and \mathbf{r} , then this expression corresponds to a high dimensional integral over all possible connections in the intervals between these two points (Fig. 10.1).

If we consider a single interval,

$$K(\mathbf{r}_j, \mathbf{r}_{j-1}; t_j - t_{j-1}) = \langle \mathbf{r}_j | e^{-\frac{i}{\hbar} \hat{H}(t_j - t_{j-1})} | \mathbf{r}_{j-1} \rangle, \quad (10.13)$$

where $t_j > t_{j-1}$ by definition. We now insert an identity operator in the momentum representation (3.72) and get for ϵ small enough,

$$\begin{aligned} K(\mathbf{r}_j, \mathbf{r}_{j-1}; t_j - t_{j-1}) &\approx \int \frac{d^3 p}{(2\pi\hbar)^3} \langle \mathbf{r}_j | \mathbf{p} \rangle e^{-\frac{i}{\hbar} H(\mathbf{p}, \mathbf{r}_j)(t_j - t_{j-1})} \langle \mathbf{p} | \mathbf{r}_{j-1} \rangle \\ &= \int \frac{d^3 p}{(2\pi\hbar)^3} e^{-\frac{i}{\hbar} H(\mathbf{p}, \mathbf{r}_j)(t_j - t_{j-1}) + \frac{i}{\hbar} \mathbf{p} \cdot (\mathbf{r}_j - \mathbf{r}_{j-1})}, \end{aligned} \quad (10.14)$$

where we take the following approximation:

$$\begin{aligned} \langle \mathbf{r}_j | e^{-\frac{i}{\hbar} \hat{H}\epsilon} | \mathbf{p} \rangle \langle \mathbf{p} | \mathbf{r}_{j-1} \rangle &\approx \langle \mathbf{r}_j | 1 - \frac{i}{\hbar} \hat{H}\epsilon | \mathbf{p} \rangle \langle \mathbf{p} | \mathbf{r}_{j-1} \rangle \\ &= \langle \mathbf{r}_j | \mathbf{p} \rangle \left[1 - \frac{i\epsilon}{\hbar} H(\mathbf{p}, \mathbf{r}_j) \right] \langle \mathbf{p} | \mathbf{r}_{j-1} \rangle \\ &\approx \langle \mathbf{r}_j | \mathbf{p} \rangle e^{-\frac{i}{\hbar} \epsilon H(\mathbf{p}, \mathbf{r}_j)} \langle \mathbf{p} | \mathbf{r}_{j-1} \rangle. \end{aligned} \quad (10.15)$$

Here $H(\mathbf{p}, \mathbf{r})$ is no longer an operator, but the Hamilton function from classical mechanics. For example,

$$H(\mathbf{p}, \mathbf{r}) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}). \quad (10.16)$$

With this we can perform the momentum integration (like in section 2.2 for the derivation of the free particle propagator (2.27)) and we get

$$K(\mathbf{r}_j, \mathbf{r}_{j-1}; t_j - t_{j-1}) = \left(\frac{m}{2\pi i \hbar \epsilon} \right)^{3/2} e^{\frac{i}{\hbar} S_{kl}(\mathbf{r}_j - \mathbf{r}_{j-1})}, \quad (10.17)$$

where

$$S_{kl}(\mathbf{r}_j, \mathbf{r}_{j-1}) = \epsilon \left[\frac{m}{2} \left(\frac{\mathbf{r}_j - \mathbf{r}_{j-1}}{\epsilon} \right)^2 - V(\mathbf{r}_j) \right]. \quad (10.18)$$

This is the classical action for the straight path from \mathbf{r}_{j-1} to \mathbf{r}_j during a time interval of length ϵ , under the assumption that the potential along the path remains constant and equal to its initial value $V(\mathbf{r}_j)$:

$$S_{kl}(\mathbf{r}_j, \mathbf{r}_{j-1}) \approx \int_{t_j-\epsilon}^{t_j} dt \mathcal{L}(\mathbf{r}, \dot{\mathbf{r}}), \quad (10.19)$$

where \mathcal{L} is the Lagrange function:

$$\mathcal{L}(\mathbf{r}, \dot{\mathbf{r}}) = \frac{m}{2} \dot{\mathbf{r}}^2 - V(\mathbf{r}). \quad (10.20)$$

The relation between (10.18) and (10.19) becomes clear, if we assume that the limit

$$\frac{\mathbf{r}_j - \mathbf{r}_{j-1}}{\epsilon} \rightarrow \dot{\mathbf{r}}_j \quad (10.21)$$

holds. For this reason we take shorter and shorter intervals ($\epsilon \rightarrow 0$) and write (10.12) as

$$K(\mathbf{r}, \mathbf{r}'; t - t') \propto \int \mathcal{D}^3 \bar{\mathbf{r}} e^{\frac{i}{\hbar} S_{kl}[\bar{\mathbf{r}}; t - t']} . \quad (10.22)$$

This is an abbreviated notation with the following meaning: in order to determine K we have to first calculate the phase factor $\exp(iS_{kl}[\bar{\mathbf{r}}; t - t']/\hbar)$, with

$$S_{kl}[\bar{\mathbf{r}}; t - t'] = \int_{t'}^t dt \mathcal{L}(\bar{\mathbf{r}}, \dot{\bar{\mathbf{r}}}), \quad (10.23)$$

for all continuous paths $\bar{\mathbf{r}}$ connecting the fixed points \mathbf{r}' and \mathbf{r} in the time $t - t'$ and then integrate over all possible paths (Fig. 10.2). This is called *path integral*. The continuity of the paths is an important point, which justifies (10.19) and (10.21). However, this continuity is an assumption which is not necessarily guaranteed, but in most practical cases is not a problem.

This formulation of quantum mechanics goes back to Feynman and has turned out to be a very useful tool in many areas of quantum field theory¹. However, since the computation of $K(\mathbf{r}, \mathbf{r}'; t - t')$ involves a complete solution of the quantum mechanical model, the propagator K is known exactly only in few cases. An example is the free particle, which we already considered in chapter 2. However, approximate solutions are possible in many cases. We now apply the philosophy of the path integrals to an important phenomenon of quantum mechanics: the *Aharonov-Bohm effect* (1959).

An interesting interference phenomenon is found when a charged particle is studied in a magnetic field. We consider as experimental setup (Fig. 10.3) a double slit

¹Literature: R.P. Feynman and A.R. Hibbs: *Quantum Mechanics and Path Integrals*, McGraw Hill; H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics and Financial Markets*, World Scientific.

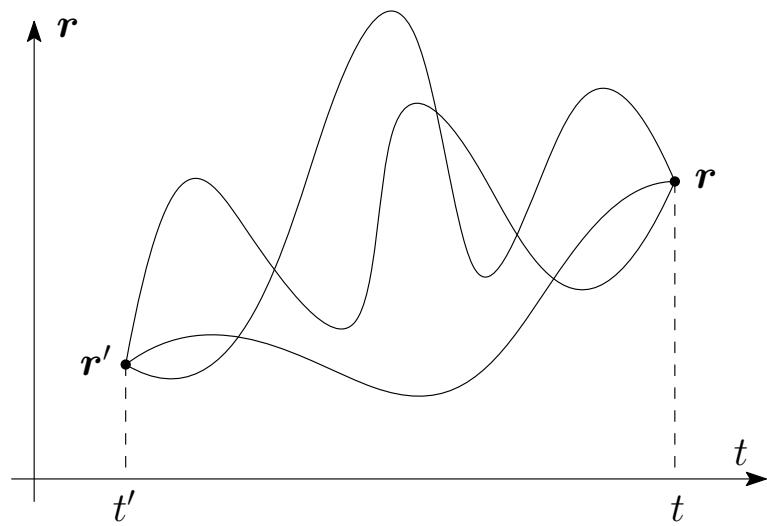


Figure 10.2: Continuous paths from (\mathbf{r}', t') to (\mathbf{r}, t) .

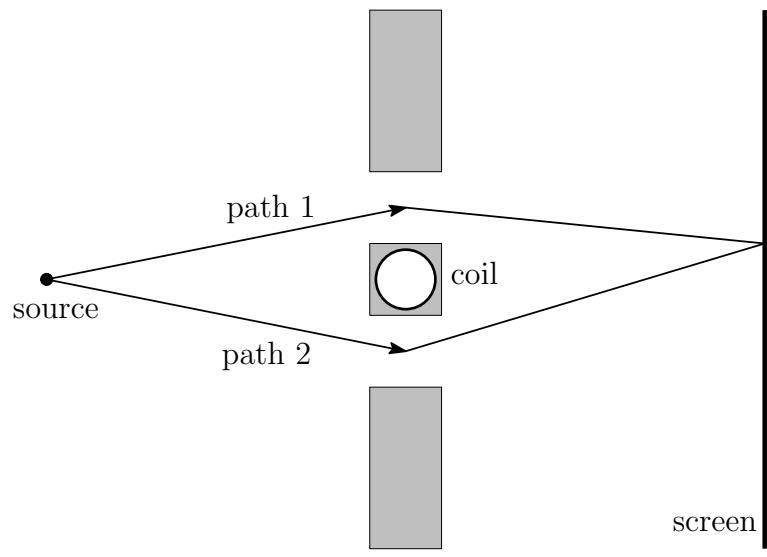


Figure 10.3: Two slits experiment with a coil between the paths.

between source (\mathbf{r}_Q) and screen (\mathbf{r}_S). Thus there are two types of paths, each through one of the two slits 1 or 2.

A magnetic coil is now inserted in such a way that the two types of path pass it on the left and on the right side, respectively. This problem can now be considered qualitatively very simply in the path integral formalism. From classical mechanics we know the Lagrange function

$$\mathcal{L} = \frac{m}{2}\dot{\mathbf{r}}^2 + \frac{e}{c}\mathbf{A}(\mathbf{r}) \cdot \dot{\mathbf{r}}, \quad (10.24)$$

where e is the charge of the particle, m its mass and \mathbf{A} the vector potential. With

$$\int dt \mathbf{A}(\bar{\mathbf{r}}) \cdot \dot{\mathbf{r}} = \int_{\text{path}} d\mathbf{s} \cdot \mathbf{A}(\bar{\mathbf{r}}) \quad (10.25)$$

we get for the two types of path ($j = 1, 2$):

$$K_j(\mathbf{r}_S, \mathbf{r}_Q; t) = K_j^{(0)}(\mathbf{r}_S, \mathbf{r}_Q; t) \exp\left(i\frac{e}{\hbar c} \int_{\text{path } j} d\mathbf{s} \cdot \mathbf{A}(\bar{\mathbf{r}})\right) = K_j^{(0)} e^{i\alpha_j}. \quad (10.26)$$

Here $K_j^{(0)}$ is the propagator of the free particle without magnetic field, and $e^{i\alpha_j}$ includes the effects of the field. The total propagator of both paths is the sum

$$K(\mathbf{r}_S, \mathbf{r}_Q; t) = K_1^{(0)} e^{i\alpha_1} + K_2^{(0)} e^{i\alpha_2} = K_1^{(0)} e^{i\alpha_1} + K_2^{(0)} e^{i\alpha_1} e^{i(\alpha_2 - \alpha_1)} = K'_1 + K'_2 e^{i(\alpha_2 - \alpha_1)}, \quad (10.27)$$

where we absorbed the phase factor $e^{i\alpha_1}$ in K'_j . In the interference of the paths there is now the phase difference $\alpha_2 - \alpha_1$, which is determined by the vector potential. It is easy to see that

$$\alpha_2 - \alpha_1 = \frac{e}{\hbar c} \left(\int_{\text{path } 2} - \int_{\text{path } 1} \right) d\mathbf{s} \cdot \mathbf{A}(\bar{\mathbf{r}}) = \frac{e}{\hbar c} \oint d\mathbf{s} \cdot \mathbf{A}(\bar{\mathbf{r}}). \quad (10.28)$$

With Stokes' theorem, one can show that the integral

$$\oint d\mathbf{s} \cdot \mathbf{A} = \int_{\text{surface}} d\mathbf{S} \cdot (\nabla \times \mathbf{A}) = \int_{\text{surface}} d\mathbf{S} \cdot \mathbf{B} = \Phi, \quad (10.29)$$

gives the magnetic flux Φ which is enclosed between the two paths. It follows that the phase difference is proportional to this flux:

$$\alpha_2 - \alpha_1 = \frac{e}{\hbar c} \Phi = 2\pi \frac{\Phi}{\Phi_0}, \quad (10.30)$$

where $\Phi_0 = hc/e$ is the flux quantum. Now we observe that for

$$\alpha_2 - \alpha_1 = 2\pi n, \quad n = 0, \pm 1, \pm 2, \dots \quad (10.31)$$

the magnetic field has no influence on the interference, since the phase difference is a multiple of 2π . Thus the interference pattern changes periodically with the flux quantum Φ_0 as period, which is 4.135×10^{-15} Vs for the charge of an electron.

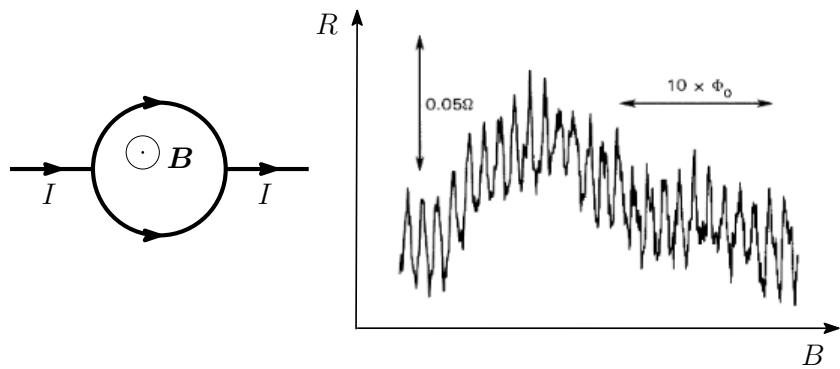


Figure 10.4: Aharonov-Bohm oscillations of the resistance in a ring.

An extremely surprising aspect is that this effect depends only on the magnetic flux enclosed by the two paths. The interference oscillations take place even if the particle trajectories never pass through a region of finite magnetic field.

There are many experimental verifications of the Aharonov-Bohm effect. One example is the oscillating magnetoresistance of mesoscopic rings in magnetic fields² (Fig. 10.4). The macroscopic flux quantization in superconducting rings is an equivalent phenomenon.

²“Observation of h/e Aharonov-Bohm Oscillations in Normal-Metal Rings”, R.A. Webb et al., Physical Review Letters **54**, 2696 (1985)

Appendix A

δ -distributions

Since δ -distributions are an important tool in quantum mechanics, we will summarize here some of their properties in the one-dimensional case. First, $\delta(x - x')$ as a “function” vanishes everywhere except for $x = x'$, where it is infinite. The defining property of the δ -distribution is

$$\int_{-\infty}^{+\infty} dx' f(x') \delta(x - x') = f(x), \quad (\text{A.1})$$

where f is an arbitrary at x continuous function. For $f \equiv 1$:

$$\int_{-\infty}^{+\infty} dx \delta(x - x') = 1. \quad (\text{A.2})$$

Furthermore, the relation

$$\delta(g(x)) = \sum_k \frac{\delta(x - x_k)}{\left| \frac{dg}{dx} \Big|_{x=x_k} \right|} \quad (\text{A.3})$$

holds, where the sum runs over all zeros x_k of g , i.e., $g(x_k) = 0$.

The δ -distributions appear frequently in connection with Fourier transforms,

$$\int dx e^{-\frac{i}{\hbar}(p-p')x} = 2\pi\hbar \delta(p - p'), \quad (\text{A.4})$$

$$\int \frac{dp}{2\pi\hbar} e^{\frac{i}{\hbar}p(x-x')} = \delta(x - x'). \quad (\text{A.5})$$

The δ -distribution can be written as limit of smooth normalized functions, for example as limit of a Gaussian,

$$\frac{1}{\sqrt{2\pi d}} e^{-\frac{(x-x')^2}{2d^2}} \xrightarrow{d \rightarrow 0} \delta(x - x'), \quad (\text{A.6})$$

where the limit $d \rightarrow 0$ gives rise to an ever tighter and higher Gauss curve.

Finally, in higher dimensions the distribution is simply the product of the individual components, e.g.

$$\delta^{(3)}(\mathbf{r} - \mathbf{r}') = \delta(x - x')\delta(y - y')\delta(z - z'), \quad (\text{A.7})$$

as it also results naturally from the definition with the Fourier transform or the Gaussian.

Appendix B

Spherical Bessel functions

The solutions of the differential equation

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} + 1 \right] f(\rho) = 0 \quad (\text{B.1})$$

are generally called spherical Bessel functions. We will summarize here some of their properties.

The spherical Bessel functions of the first kind (or simply spherical Bessel functions) $j_l(\rho)$ are related to the usual Bessel functions of the first kind $J_\nu(\rho)$ through

$$j_l(\rho) = \left(\frac{\pi}{2\rho} \right)^{\frac{1}{2}} J_{l+\frac{1}{2}}(\rho). \quad (\text{B.2})$$

Alternatively, they are given by

$$j_l(\rho) = (-\rho)^l \left(\frac{1}{\rho} \frac{d}{d\rho} \right)^l \frac{\sin \rho}{\rho}. \quad (\text{B.3})$$

The functions $j_l(\rho)$ are regular for $\rho \rightarrow 0$ with

$$j_l(\rho) = \frac{\rho^l}{(2l+1)!!} \left(1 - \frac{\frac{1}{2}\rho^2}{1!(2l+3)} + \frac{\left(\frac{1}{2}\rho^2\right)^2}{2!(2l+3)(2l+5)} - \dots \right), \quad (\text{B.4})$$

where $n!! = n \cdot (n-2) \cdot (n-4) \dots$. Their asymptotic behavior for $\rho \rightarrow \infty$ is

$$j_l(\rho) \approx \frac{1}{\rho} \sin \left(\rho - \frac{\pi l}{2} \right). \quad (\text{B.5})$$

The functions for $l = 0, 1, 2$ are

$$j_0(\rho) = \frac{\sin \rho}{\rho}, \quad (\text{B.6})$$

$$j_1(\rho) = \frac{\sin \rho - \rho \cos \rho}{\rho^2}, \quad (\text{B.7})$$

$$j_2(\rho) = \frac{(3 - \rho^2) \sin \rho - 3\rho \cos \rho}{\rho^3}. \quad (\text{B.8})$$

The spherical Bessel functions of the second kind (or spherical Neumann functions) $n_l(\rho)$ are defined by

$$n_l(\rho) = (-1)^{l+1} \left(\frac{\pi}{2\rho} \right)^{\frac{1}{2}} J_{-l-\frac{1}{2}}(\rho), \quad (\text{B.9})$$

or alternatively with

$$n_l(\rho) = -(-\rho)^l \left(\frac{1}{\rho} \frac{d}{d\rho} \right)^l \frac{\cos \rho}{\rho}. \quad (\text{B.10})$$

These functions are not regular for $\rho \rightarrow 0$, since

$$n_l(\rho) = -\frac{(2l-1)!!}{\rho^{l+1}} \left(1 - \frac{\frac{1}{2}\rho^2}{1!(1-2l)} + \frac{\left(\frac{1}{2}\rho^2\right)^2}{2!(1-2l)(3-2l)} - \dots \right). \quad (\text{B.11})$$

Their asymptotic behavior for $\rho \rightarrow \infty$ is

$$n_l(\rho) \approx -\frac{1}{\rho} \cos \left(\rho - \frac{\pi l}{2} \right). \quad (\text{B.12})$$

The functions for $l = 0, 1, 2$ are

$$n_0(\rho) = -\frac{\cos \rho}{\rho}, \quad (\text{B.13})$$

$$n_1(\rho) = -\frac{\cos \rho + \rho \sin \rho}{\rho^2}, \quad (\text{B.14})$$

$$n_2(\rho) = -\frac{(3-\rho^2) \cos \rho + 3\rho \sin \rho}{\rho^3}. \quad (\text{B.15})$$

The spherical Hankel functions $h_l^{(1)}(\rho)$ und $h_l^{(2)}(\rho)$ are given by

$$h_l^{(1)}(\rho) = j_l(\rho) + i n_l(\rho), \quad (\text{B.16})$$

$$h_l^{(2)}(\rho) = j_l(\rho) - i n_l(\rho) = h_l^{(1)}(\rho)^*. \quad (\text{B.17})$$

They are singular for $\rho \rightarrow 0$, because of $n_l(\rho)$, and their asymptotic behavior for $\rho \rightarrow \infty$ is

$$h_l^{(1)}(\rho) \approx -\frac{i}{\rho} e^{i(\rho-l\frac{\pi}{2})}, \quad (\text{B.18})$$

$$h_l^{(2)}(\rho) \approx \frac{i}{\rho} e^{-i(\rho-l\frac{\pi}{2})}. \quad (\text{B.19})$$

Appendix C

Groups and representation theory

A *group* \mathcal{G} is a set with a binary operation $*$, which satisfy the following axioms:

$$\forall g_1, g_2 \in \mathcal{G} : g_1 * g_2 = g_3 \in \mathcal{G} \quad (\text{closedness}) \quad (\text{C.1})$$

$$\exists e \in \mathcal{G} \forall g \in \mathcal{G} : g * e = e * g = g \quad (\text{identity element}) \quad (\text{C.2})$$

$$\forall g \in \mathcal{G} \exists g^{-1} \in \mathcal{G} : g * g^{-1} = g^{-1} * g = e \quad (\text{inverse element}) \quad (\text{C.3})$$

$$\forall g_1, g_2, g_3 \in \mathcal{G} : g_1 * (g_2 * g_3) = (g_1 * g_2) * g_3 \quad (\text{associativity}) \quad (\text{C.4})$$

We distinguish between Abelian and non-Abelian groups. For an Abelian group the property

$$\forall g_1, g_2 \in \mathcal{G} : g_1 * g_2 = g_2 * g_1 \quad (\text{commutativity}) \quad (\text{C.5})$$

also holds. This property does not apply to non-Abelian groups.

The elements of \mathcal{G} can induce a transformation on a vector space \mathcal{V} , by assigning to each element $g \in \mathcal{G}$ an operator $\widehat{U}(g)$ acting on the vectors of \mathcal{V} (for finite dimensional vector spaces one can identify $\widehat{U}(g)$ with a matrix, if one chooses a basis on \mathcal{V}). The assignment $g \mapsto \widehat{U}(g)$ must respect the group structure, i.e., if one performs two transformations in a row, the composition law

$$\widehat{U}(g_1)\widehat{U}(g_2) = \widehat{U}(g_1 * g_2) \quad (\text{C.6})$$

must hold. It follows:

$$\widehat{U}(e) = \widehat{1} \quad \text{and} \quad \widehat{U}(g^{-1}) = \widehat{U}(g)^{-1}, \quad (\text{C.7})$$

i.e., the operators $\widehat{U}(g)$ also constitute a group. Such an assignment $g \mapsto \widehat{U}(g)$ is called *representation*. The dimension of the vector space \mathcal{V} is also called *dimension of the representation*. We consider here only unitary representations, i.e., the operators $\widehat{U}(g)$ are unitary:

$$\widehat{U}(g)^\dagger \widehat{U}(g) = \widehat{1}, \quad \forall g \in \mathcal{G}, \quad (\text{C.8})$$

or, to put it another way, $\widehat{U}(g^{-1}) = \widehat{U}(g)^{-1} = \widehat{U}(g)^\dagger$.

A subspace $\mathcal{W} \subset \mathcal{V}$ is invariant under the representation if $\widehat{U}(g)\mathcal{W} \subset \mathcal{W}$ for all $g \in \mathcal{G}$. The whole vector space \mathcal{V} and the trivial subspace $\{|0\rangle\}$ are always invariant. If the vector space \mathcal{V} has other invariant subspaces, then the representation is called

reducible, otherwise *irreducible*. If one thinks of the operators $\widehat{U}(g)$ as matrices, then a representation is reducible if there exists an (orthonormal) basis of \mathcal{V} such that all $\widehat{U}(g)$ decompose into the same block diagonal form. One then writes the representation

$$\widehat{U}(g) = \left(\begin{array}{c|c} \widehat{U}_1(g) & 0 \\ \hline 0 & \widehat{U}_2(g) \end{array} \right) \quad (\text{C.9})$$

as direct sum

$$\widehat{U}(g) = \widehat{U}_1(g) \oplus \widehat{U}_2(g). \quad (\text{C.10})$$

For compact groups¹, one can successively reduce each finite dimensional representation, until one can write it as a direct sum of irreducible representations. Thus the irreducible representations of a group form the building blocks for all other representations and it is convenient to classify them.

Some facts about irreducible representations:

- There is always a trivial representation, in which each element $g \in \mathcal{G}$ is mapped to the number 1. This representation is one-dimensional.
- For an Abelian group all irreducible representations are one-dimensional.
- The basis vectors of different irreducible representations are always orthogonal to each other.

In quantum mechanics the Hilbert space \mathcal{H} is the vector space of all quantum states of a system. Transformations arising from a symmetry of the system form a group. The irreducible representations of this group correspond to Hilbert subspaces which are invariant under these transformations. In particular, all states in an invariant subspace have the same energy, because the operators $\widehat{U}(g)$ commutes with the Hamilton operator \widehat{H} . Therefore, the dimension of the irreducible representations is equivalent to the (minimal) degeneracy of the energy eigenstates.

¹Like for example the special orthogonal group $\text{SO}(n) = \{O \in \mathbb{R}^{n \times n} | O^T O = 1, \det O = 1\}$ and the special unitary group $\text{SU}(n) = \{U \in \mathbb{C}^{n \times n} | U^\dagger U = 1, \det U = 1\}$.

Appendix D

Pauli matrices

The Pauli matrices,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (\text{D.1})$$

have a number of properties that are important in connection with $s = 1/2$ spins. Together with the unit matrix σ_0 ,

$$\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad (\text{D.2})$$

they are a basis of the vector space of 2×2 complex-valued matrices:

$$A = \alpha_0\sigma_0 + \boldsymbol{\alpha} \cdot \boldsymbol{\sigma} = \alpha_0\sigma_0 + \sum_{a=x,y,z} \alpha_a\sigma_a, \quad (\text{D.3})$$

with $\alpha_0, \alpha_a \in \mathbb{C}$. Furthermore

$$\sigma_a^2 = \sigma_0, \quad (\text{D.4})$$

holds, their traces are

$$\text{Sp } \sigma_x = \text{Sp } \sigma_y = \text{Sp } \sigma_z = 0, \quad \text{Sp } \sigma_0 = 2, \quad (\text{D.5})$$

and the determinants give

$$\det \sigma_x = \det \sigma_y = \det \sigma_z = -1, \quad \det \sigma_0 = 1. \quad (\text{D.6})$$

The commutation and anticommutation relations of σ_x and σ_y are

$$[\sigma_x, \sigma_y] = \sigma_x\sigma_y - \sigma_y\sigma_x = 2i\sigma_z, \quad \{\sigma_x, \sigma_y\} = \sigma_x\sigma_y + \sigma_y\sigma_x = 0, \quad (\text{D.7})$$

which leads to

$$\sigma_x\sigma_y = -\sigma_y\sigma_x = i\sigma_z. \quad (\text{D.8})$$

Analogously, for all cyclic permutations of (x, y, z) ,

$$\sigma_y\sigma_z = -\sigma_z\sigma_y = i\sigma_x, \quad \text{and} \quad \sigma_z\sigma_x = -\sigma_x\sigma_z = i\sigma_y. \quad (\text{D.9})$$

Furthermore $\sigma_x\sigma_y\sigma_z = i\sigma_0$ holds. One can summarize this relations in

$$\sigma_a\sigma_b = \delta_{ab}\sigma_0 + i\epsilon_{abc}\sigma_c, \quad (\text{D.10})$$

where $a = x, y, z$. From this, the following important equation can be derived:

$$(\boldsymbol{\sigma} \cdot \boldsymbol{\alpha})(\boldsymbol{\sigma} \cdot \boldsymbol{\beta}) = \sigma_0(\boldsymbol{\alpha} \cdot \boldsymbol{\beta}) + i\boldsymbol{\sigma} \cdot (\boldsymbol{\alpha} \times \boldsymbol{\beta}), \quad (\text{D.11})$$

for two vectors $\boldsymbol{\alpha}, \boldsymbol{\beta} \in \mathbb{C}^3$. Therefore, for a vector $\boldsymbol{\alpha} = \alpha\mathbf{n}$ with $|\mathbf{n}| = 1$

$$(\boldsymbol{\sigma} \cdot \boldsymbol{\alpha})^2 = \alpha^2\sigma_0 \quad (\text{D.12})$$

and, in general,

$$(\boldsymbol{\sigma} \cdot \boldsymbol{\alpha})^k = \begin{cases} \alpha^k\sigma_0, & \text{for } k \text{ even,} \\ \alpha^k(\mathbf{n} \cdot \boldsymbol{\sigma}), & \text{for } k \text{ odd.} \end{cases} \quad (\text{D.13})$$

hold. We can use it to calculate the exponential matrix $\exp(i\boldsymbol{\alpha} \cdot \boldsymbol{\sigma}/2)$ which describes rotations in spin space:

$$\begin{aligned} e^{\frac{i\boldsymbol{\alpha} \cdot \boldsymbol{\sigma}}{2}} &= \sum_{k=0}^{\infty} \frac{1}{k!} \left(\frac{i\boldsymbol{\alpha} \cdot \boldsymbol{\sigma}}{2} \right)^k \\ &= \sum_{k \text{ even}} \frac{i^k}{k!} \left(\frac{\alpha}{2} \right)^k \sigma_0 + \sum_{k \text{ odd}} \frac{i^k}{k!} \left(\frac{\alpha}{2} \right)^k (\mathbf{n} \cdot \boldsymbol{\sigma}) \\ &= \sum_{j=0}^{\infty} \frac{(-1)^j}{(2j)!} \left(\frac{\alpha}{2} \right)^{2j} \sigma_0 + i \sum_{j=0}^{\infty} \frac{(-1)^j}{(2j+1)!} \left(\frac{\alpha}{2} \right)^{2j+1} (\mathbf{n} \cdot \boldsymbol{\sigma}) \\ &= \cos\left(\frac{\alpha}{2}\right) \sigma_0 + i \sin\left(\frac{\alpha}{2}\right) (\mathbf{n} \cdot \boldsymbol{\sigma}), \end{aligned} \quad (\text{D.14})$$

where we set $k = 2j$ (with $i^k = (-1)^j$) in the first sum and $k = 2j + 1$ (with $i^k = i(-1)^j$) in the second.