

# Quantum Mechanics I (P303 / M326)

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# 1. INTRODUCTION

There are many routes towards quantum mechanics. Here, we present a short historical introduction focussing on black-body radiation. We follow a recent article by Domenico Giulini und Norbert Straumann<sup>1</sup>

## 1.1 The Radiation Laws and the Birth of Quantum Mechanics

Quantum mechanics was born on the 14th December 1900 when Max Planck explained the derivation of his radiation law at a meeting of the German Physical Society in Berlin. It was a desperate attempt to explain findings by Lummer, Pringsheim, Kurlbaum, Paschen, and Rubens who had performed precise experiments on thermal radiation of certain objects called ‘black body radiators’.

The black body radiator was a concept from the middle of the 19th century, introduced by Kirchhoff in 1859. Kirchhoff discussed the thermal equilibrium between the radiation (heat) within an arbitrarily shaped container and the walls of the container (black bodies) that completely absorb all incident radiation. The walls also emit radiation since otherwise there would be no radiation within the container at all (which contradicts experiments). The radiation inside such a cavity is called **black body radiation**.

From thermodynamics (second law) one can show that the **spectral energy density**  $u$  of black body radiation, i.e. the radiation energy per volume and per frequency interval, is only a function of the frequency  $\nu$  and the temperature  $T$  of the walls, and does not depend, e.g., on the shape of the container:

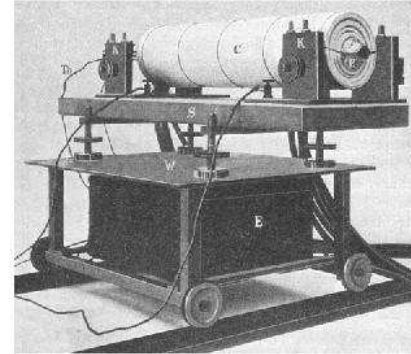
$$u = u(\nu, T) \quad \text{universal.} \quad (1.1)$$

Note:  $\int_{\nu_1}^{\nu_2} d\nu u = u(\nu, T)$  is the radiation energy within the frequency interval  $[\nu_1, \nu_2]$ .

Kirchhoff had already pointed out the importance of determining the explicit form function  $u(\nu, T)$ . Its importance should lie in the fact that it was *universal*, i.e. independent of any details of the geometry of the container. Such a universal function could be expected to contain deep physical insights about thermodynamics and radiation.

In fact, it took 40 years and the efforts of many physicists to finally find the explicit form of  $u(\nu, T)$ . After Kirchhoff’s introduction of the ‘black body’, people were wondering how to realise this theoretical concept experimentally. They first tried to blacken metallic (platinum) plates without much success. The success came by Otto Lummer and Wilhelm Wien (‘Physikalisch–Technische–Reichsanstalt’, the PTR in Berlin, a predecessor of the nowadays PTB, the German national Bureau of standards). They went back to the original definition (thermal equilibrium with the walls of the container) of the black body and argued that one should use a cavity with a small hole inside to get the black body radiation out of it, without disturbing it too much.

<sup>1</sup> Domenico Giulini und Norbert Straumann [in German] ‘Ich dachte mir nicht viel dabei’: Plancks Weg zur Strahlungsformel, Phys. Bl. 12/2000, p. 37.



**Fig. 1.1:** Lummer and Kurlbaum’s black-body experiment from 1898: platinum cylinder sheet within a ceramic tube [Phys. Bl. 12/2000, p. 43].

At that time, there was already the theoretical prediction by **Wien** who had found in 1893 a *scaling law* for  $u(\nu, T)$ , stating

$$u(\nu, T) = \nu^3 f(\nu/T) \quad (1.2)$$

with an (unknown) ‘scaling function’  $f$  of only *one* variable, i.e. the ratio  $\nu/T$ . In particular, this scaling law immediately explained the **Stefan–Boltzmann–law**

$$U(T) := \int_0^\infty d\nu u(\nu, T) = \sigma T^4, \quad \sigma = \text{const.} \quad (1.3)$$

Wien even made a suggestion for the explicit form of  $f$  in analogy to Maxwell’s velocity distribution in a gas (**Wien’s law**),

$$u(\nu, T) = \frac{4\nu^3}{c^3} b \exp\left(-\frac{a\nu}{T}\right), \quad a, b = \text{const.}, \quad (1.4)$$

(valid for large frequencies and small temperatures: quantum limit !)

where  $c$  is the speed of light. Wien’s law was compatible with the experimental results until the middle of the year 1900. Lummer and his coworker Kurlbaum had developed a very precise bolometer, based on the bolometer by Samuel P. Langley used in astrophysics from 1880. Furthermore, Lummer and his coworker Pringsheim developed black body radiators that could operate in a very large temperature range between  $-188^\circ\text{C}$  and  $1200^\circ\text{C}$ , later up to temperatures of  $1600^\circ\text{C}$ .

It turned out that Wien’s law (1.4) was quite a good description of the experimental data but there were small deviations at large temperatures. Lummer and Pringsheim again improved their experiment into the range of up to wavelengths  $\lambda = c/\nu$  of  $\lambda = 8.3\mu\text{m}$  and  $T = 1650\text{K}$ , and the deviations became even stronger. The story became even more confusing in the autumn of 1900 when Friedrich Paschen in Hannover claimed good agreement of his data with (1.4), and Max Planck also had ‘proven’ it by thermodynamic considerations.

The bomb came with new measurements by a guest scientist at the PTR (Heinrich Rubens) which extended up to  $\lambda = 50\mu\text{m}$ . The deviations from Wien’s law could not be discussed away

any longer. Rather, in the extreme long wave-length limit, Rubens found good agreement with another radiation law that had previously set up by Lord Rayleigh (**Rayleigh-Jeans-law**),

$$u(\nu, T) = \rho(\nu) \bar{E}(\nu) = \frac{8\pi\nu^2}{c^3} k_B T, \quad (1.5)$$

(valid for small frequencies and large temperatures: classical limit !)

where  $k_B$  is the Boltzmann constant. Rayleigh's law followed from the **density of states**  $\rho(\nu) = 8\pi\nu^2/c^3$  (density of electromagnetic eigenmodes per volume, polarization direction and frequency) of the electromagnetic field in a cavity, and the theorem of thermodynamics that gives each degree of freedom of an oscillation in thermal equilibrium an average energy  $\bar{E}(\nu) = k_B T$  ( $1/2k_B T$  for kinetic and potential energy each), independent of the frequency  $\nu$ .

Rubens told Planck of his observations over afternoon tea, and the same evening Planck, in a desperate attempt to 'improve' Wien's law, suggested an interpolation formula between (1.4) and (1.5), **Planck's law**

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}, \quad (1.6)$$

where the new constant  $h$  is the **Planck constant**

$$h = 6.626 \times 10^{-34} Js. \quad (1.7)$$

Planck's law turned out to give excellent agreement with all the experimental data. He solved this puzzle by the hypothesis **Planck's hypothesis**, that oscillators change their energies  $E(\nu)$  only in integer multiples of a fundamental energy unit  $\varepsilon$ . He didn't explicitly assume  $E(\nu) = n\varepsilon$  at that time, but he showed that  $\varepsilon$  must be proportional to the frequency  $\nu$ , i.e.  $\varepsilon = h\nu$ .

### 1.1.1 Remarks

1. Note that ironically, quantum mechanics was discovered via the *classical limit* of a radiation law! In fact, the Rayleigh-Jeans-law contains no Planck constant  $h$ , whereas the parameters  $a$  and  $b$  in the 19th-century 'thermodynamic' Wien law contain  $h$  and  $k_B$ , both fundamental constants in microscopic theories (although at that time, the deep physical meaning of  $a$  and  $b$  was of course not understood).

2. Nowadays, instead of  $h$  one often uses  $\hbar = h/2\pi$ . Instead of the frequency  $\nu$  one often uses the angular frequency  $\omega = 2\pi\nu$ . If  $\omega$  is used instead of  $\nu$ , the spectral energy density  $w(\omega, T)$  is defined as  $w(\omega, T)d\omega = u(\nu, T)d\nu$ . Since  $d\omega = 2\pi d\nu$ , this gives  $w(\omega, T) = \omega^2/(\pi^2 c^3) \times \hbar\omega/(\exp(\hbar\omega/kT) - 1)$ . Therefore, be careful when comparing different definitions and doing calculations because a wrong factor  $2\pi$  gives a result that is wrong by nearly one order of magnitude!

3. Cosmic black body radiation is a consequence of the 'Big Bang Model'. Measurements of the cosmic background radiation corresponding to a temperature  $T \approx 2.7K$  were performed by R. H. Dicke and co-workers.

### 1.1.2 \* Math: Density of states

A math theorem tells that for a function  $f(x)$ ,

$$\lim_{L \rightarrow \infty} \frac{1}{L} \sum_{n=0}^{\infty} f(n/L) = \int_0^{\infty} f(x) dx. \quad (1.8)$$

Assume standing waves in a box of size  $L^3$  with wave vectors

$$\mathbf{k} = (\pi n_x/L, \pi n_y/L, \pi n_z/L).$$

Assume we wish to calculate a function  $f(\mathbf{k}) = f(k)$  that only depends on the modulus of  $\mathbf{k}$ . We use

$$\lim_{L \rightarrow \infty} \frac{1}{L^3} \sum_{n_x, n_y, n_z=0}^{\infty} f(\pi n_x/L, \pi n_y/L, \pi n_z/L) = \frac{1}{\pi^3} \int_0^{\infty} f(\mathbf{k}) dk_x dk_y dk_z, \quad (1.9)$$

i.e.

$$\begin{aligned} \lim_{L \rightarrow \infty} \frac{1}{L^3} \sum_{k_x, k_y, k_z > 0} f(k) &= \frac{1}{\pi^3} \int_0^{\infty} f(k) dk_x dk_y dk_z = \frac{1}{\pi^3 2^3} \int_{-\infty}^{\infty} f(k) dk_x dk_y dk_z \\ &= \frac{1}{(2\pi)^3} \int_0^{\infty} dk 4\pi k^2 f(k) = \int_0^{\infty} dk \frac{k^2}{2\pi^2} f(k) \\ &= \int_0^{\infty} d\omega \frac{\omega^2}{2\pi^2 c^3} f(\omega) =: \int_0^{\infty} d\omega \rho(\omega) f(\omega) \\ \rho(\omega) &:= \frac{\omega^2}{2\pi^2 c^3}. \end{aligned} \quad (1.10)$$

Here,  $\rho(\omega)$  is the density of states if there was only one polarization direction per possible 'state' (wave vector  $\mathbf{k}$ ). If there are two polarization directions, like for unpolarized light, the density of states is twice as large, i.e.  $\rho(\omega) := \frac{\omega^2}{\pi^2 c^3}$ .

## 1.2 Waves, particles, and wave packets

### 1.2.1 Introduction

After our relatively detailed historic introduction above, we only shortly touch the important other findings that lead to quantum mechanics. The first is the **photoelectric effect**, discovered by Hertz in 1887 in tin plates that got positively charged when irradiated with UV light. Electrons are emitted from a metal surface only if the frequency is above a certain limit. Also, experiments by Philipp Lenard<sup>2</sup> showed that the kinetic energy  $(1/2)mv^2$  is independent of the intensity of the radiation. Einstein explained this effect in 1905 by introducing discrete quanta of light, i.e. **photons**, with energy

$$E = h\nu, \quad (1.11)$$

which are absorbed in order to kick an electron out of the metal. Energy conservation requires  $E = E_{\text{kin}} + W$ , where  $W$  the 'work function', i.e. the energy to get the electrons out of the metal, and  $E_{\text{kin}} = \frac{1}{2}m_e v^2$  is the additional kinetic energy of the electron (mass  $m_e$ ) when it has a finite velocity  $v$ . On the other hand, the general expression for the total energy of a particle is

$$E^2 = (mc^2)^2 + p^2 c^2, \quad (1.12)$$

<sup>2</sup> Philipp Lenard won the Nobel prize in 1905 but later became an enemy of Einstein and a strong anti-Semitic Nazi supporter. He published a four-volume physics text book with the title 'German Physics'.

and for photons that move with the velocity of light  $c$  the mass (rest mass)  $m$  must be zero. This yields

$$pc = h\nu \rightsquigarrow p = h/\lambda. \quad (1.13)$$

Introducing the wave vector  $\mathbf{k}$  with  $|\mathbf{k}| = 2\pi/\lambda$ , pointing in the same direction as  $\mathbf{p}$ , this establishes the relation between momentum and wave vector,

$$\mathbf{p} = \hbar\mathbf{k} \quad \text{for photons.} \quad (1.14)$$

In particular, the photoelectric effect showed that light has a particle aspect. On the other hand, it was known that interference etc. were consequences of the wave properties of light.

In 1923, this **particle–wave duality** was extended to matter, i.e. massive objects, by de Broglie. Wave properties of matter had already been discussed in the 19th century by Hamilton. It was known that geometrical optics could be derived from the wave theory of light (Eikonal equation). In a similar way, there was an **Eikonal equation** in a branch of theoretical mechanics called **Hamilton–Jacobi theory**. By this one could speculate that classical mechanics had to be a limiting case of some more complete theory (quantum mechanics), in the same spirit as geometrical optics is the limiting case of wave theory.

A non–relativistic, freely moving particle of mass  $m$  and momentum  $p$  has a kinetic energy  $E = p^2/2m$ . If the particle–wave duality can be extended from photons to massive objects, this particle also can be considered as a wave, and one could postulate the same relation between momentum and wave vector as for photons,

$$\mathbf{p} = \hbar\mathbf{k} \quad \text{for massive particles.} \quad (1.15)$$

Further experimental hints stem from experiments where electrons are scattered at crystal surfaces and behave like waves (Davisson, Germer).

The de–Broglie relation means that a particle can be described as a wave with wave vector  $\mathbf{k}$  and angular frequency  $\omega$ . The simplest form of such a wave is a plane wave

$$\Psi(\mathbf{x}, t) = Ae^{i(\mathbf{k}\mathbf{x} - \omega t)}, \quad (1.16)$$

but how should this quantity (which is a complex and not a real number) describe a particle? One could form real superpositions into sin and cos, but even then this ‘particle’ would be extended from minus to plus infinity which seems absolutely awkward. Intuition tells one that a particle should be localized in space; at any fixed time  $t_0$  it should be at some point  $\mathbf{x}_0$  somewhere in space. Still, going ahead with the wave concept of matter, one can form **superpositions** of plane waves.

### 1.2.2 The wave packet

Let us come back to de Broglie’s idea to describe a particle as a wave or better as a superposition of waves. We assume that a particle with energy  $E = p^2/2m$  can be described by a function that is a superposition of plane waves,

$$\Psi(x, t) = \int_{-\infty}^{\infty} dka(k)e^{i(kx - \omega(k)t)}, \quad \hbar\omega(k) = E = \hbar^2k^2/(2m). \quad (1.17)$$

We have used the relation between momentum and wave vector,  $p = \hbar k$ , and the relation between energy and angular frequency,  $E = \hbar\omega$ . As with waves, the angular frequency  $\omega$  in

general depends on the wave length and therefore  $\omega = \omega(k)$ . For simplicity, we adopted a one–dimensional version. Note that the time evolution of a *single* plane wave  $e^{i(kx - \omega t)}$  goes with the minus sign. We would like to know the time evolution of the function  $\Psi(x, t)$ , i.e. to find its **equation of motion**. Equations of motion often represent fundamental laws in physics, like Newton’s  $F = ma$ , which is a second order differential equation  $\ddot{x} = (1/m)F(x)$ . We therefore differentiate (1.17) with respect to time (we write  $\partial_t$  for  $\partial/\partial t$  etc.

$$\begin{aligned} i\hbar\partial_t\Psi(x, t) &= \int dka(k)\hbar\omega(k)e^{i(kx - \omega(k)t)} = \int dka(k)E(k)e^{i(kx - \omega(k)t)} = \\ &= \int dka(k)\frac{\hbar^2k^2}{2m}e^{i(kx - \omega(k)t)} = -\frac{\hbar^2\partial_x^2}{2m}\int dka(k)e^{i(kx - \omega(k)t)} = \\ &= -\frac{\hbar^2\partial_x^2}{2m}\Psi(x, t). \end{aligned} \quad (1.18)$$

So far we have only considered a particle that only has kinetic energy  $E = p^2/2m = E(k) = (\hbar k)^2/2m$ . In general, a particle can have both kinetic energy and **potential energy**  $V(x)$ . Example: A harmonic oscillator with angular frequency  $\omega$  and mass  $m$  in one dimension has the potential energy  $V(x) = (1/2)m\omega^2x^2$ .

We now *postulate* that the above equation for a free particle (zero potential energy),

$$i\hbar\partial_t\Psi(x, t) = \int dka(k)E(k)e^{i(kx - \omega(k)t)},$$

has to be *generalized* by replacing  $E(k)$  with the total energy  $E(k) + V(x)$  for a particle in a non–zero potential. Then, the equation of motion becomes

$$\begin{aligned} i\hbar\partial_t\Psi(x, t) &= \int dka(k)[E(k) + V(x)]e^{i(kx - \omega(k)t)} = \\ &= \left[-\frac{\hbar^2\partial_x^2}{2m} + V(x)\right]\Psi(x, t). \end{aligned} \quad (1.19)$$

The equation

$$i\hbar\frac{\partial}{\partial t}\Psi(x, t) = \left[-\frac{\hbar^2\partial_x^2}{2m} + V(x)\right]\Psi(x, t) \quad (1.20)$$

is called **Schrödinger equation** and is one of the most important equations of physics at all. We only have given the one–dimensional version of it so far, the generalization to two or three dimensions is not difficult: the variables  $x$  and  $k$  become vectors  $\mathbf{x}$  and  $\mathbf{k}$ . Instead of the **differential operator**  $\partial_x^2$ , one has  $\partial_x^2 + \partial_y^2$  in two or  $\partial_x^2 + \partial_y^2 + \partial_z^2$  in three dimensions. This is nothing else but the **Laplace operator**  $\Delta = \partial_x^2 + \partial_y^2 + \dots$ . The Schrödinger equation reads

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x}, t) = \left[-\frac{\hbar^2\Delta}{2m} + V(\mathbf{x})\right]\Psi(\mathbf{x}, t). \quad (1.21)$$

## 1.3 Interpretation of the Wave Function

### 1.3.1 Interference experiments

Davisson and Germer performed experiments where electrons were scattered at the surface of a crystal. They observed interference, similar to the scattering of light, e.g. X-rays. In particular, destructive interference cannot be explained in a corpuscular picture.

After Schrödinger had set up his equation for the **wave function**  $\Psi(x, t)$ , it was not clear at all how to interpret this object. We have seen that as a superposition of plane waves,  $\Psi(x, t)$  obviously must have wave properties. On the other hand, the photo effect and other effects like the Compton effect showed that electrons act as particles as well.

It became clear that a statistical interpretation of  $\Psi(x, t)$  was a consistent way to combine both wave and particle aspects within one picture. In fact, in the experiments where interference was observed, always many particles were involved. This does not mean that the interaction between the particles is required to lead to interference. Even at very low intensities of particle beams, where in the extreme case only one electron at a time scatters from the surface of the crystal, in the end an interference pattern is observed on a screen (or when plotting a histogram of the electrons counted by different detectors). This suggested that the physical content of the wave function is related to a **probability**. It is clear, on the other hand, that a probability must be positive. One could imagine this probability as a kind of intensity which for waves  $\Psi$  is given by  $|\Psi|^2$ . This is only a heuristic argument, one could argue that also  $|\Psi|^4$  could do it. We therefore have another look at the Schrödinger equation.

### 1.3.2 First Axiom

**Axiom 1:** The wave function  $\Psi(\mathbf{x}, t)$  for a particle with mass  $m$  moving in a potential  $V(\mathbf{x})$  obeys the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{x}, t) = \left[ -\frac{\hbar^2 \Delta}{2m} + V(\mathbf{x}) \right] \Psi(\mathbf{x}, t). \quad (1.22)$$

$|\Psi(\mathbf{x}, t)|^2 d^3x$  is the probability for the particle to be in the (infinitesimal small) volume  $d^3x$  around  $\mathbf{x}$  at time  $t$ . The probability  $P(\Omega)$  for the particle to be in a finite volume  $\Omega$  of space is given by the integral over this volume:

$$P(\Omega) = \int_{\Omega} d^3x |\Psi(\mathbf{x}, t)|^2. \quad (1.23)$$

The probability to find the particle *somewhere* in space must be one and hence

$$\int_{R^3} d^3x |\Psi(\mathbf{x}, t)|^2 = 1. \quad (1.24)$$

Remarks:

1. In formulating this axiom, we already made an abstract assumption of one and only one particle that can be somewhere in space. Only the interaction with the potential  $V(\mathbf{x})$  is included, which is assumed to be a given function of  $\mathbf{x}$ . This potential can be created by, e.g., electric fields and therewith indirectly by the interactions with other particles which are, however, are not included explicitly.

2. There are no relativistic effects included here.

3. The normalization condition (1.24) is necessary for an interpretation of  $|\Psi|^2$  as a probability density.  $\Psi$  must be **square integrable**. Functions  $\Psi$  that are square integrable belong to an infinite dimensional vector space of functions, the Hilbert space  $L^2(R^3)$ . The **Hilbert space** is a central object in the mathematical theory of quantum mechanics. Basically, it replaces the phase space of points  $(x, p)$  from classical mechanics.



**Fig. 1.2:** In this example, the random variable  $x$  is the distance  $x = r$  to the center.

### 1.3.3 Probability densities

In the following, we will introduce some basic mathematical concepts that are required to formulate the probabilistic aspect of the wave function.

Let  $x \in [-\infty, \infty]$  be a random variable, e.g. the outcome of a measurement. The **probability density**  $\rho(x)$  of  $x$  is defined in the following way:  $\rho(x)dx$  is the probability that  $x$  lies in  $[x, x + dx]$ . Clearly,  $\rho(x)$  has to be normalized, i.e.  $\int_{-\infty}^{\infty} dx \rho(x) = 1$ . Alternatively, one often uses the following

**Definition 1 (Probability Density).** Let  $P(a \leq x \leq b)$  be the probability for the random variable  $x$  to be in the interval  $[a, b]$ . We define the **probability density**  $\rho(x)$  by

$$P(a \leq x \leq b) = \int_a^b dx \rho(x). \quad (1.25)$$

Remarks:

- $\rho(x) \geq 0$ .
- $\int_{-\infty}^{\infty} dx \rho(x) \equiv P(-\infty \leq x \leq \infty) = 1$ .
- $P(-\infty \leq x' \leq x)$  is called *distribution function*.

### 1.3.4 Example: Gauss distribution

**Definition 2 (Gauss Distribution).** The function

$$\rho(x) \equiv \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-x_0)^2}{2\sigma^2}\right) \quad (1.26)$$

is the probability density of the Gauss distribution with parameters  $x_0$  and  $\sigma > 0$ .

We have the following important integral (Gauss integral):

$$\int_{-\infty}^{\infty} dx e^{-ax^2+bx} = \sqrt{\frac{\pi}{a}} \exp\left(\frac{b^2}{4a}\right). \quad (1.27)$$

Proof: First consider  $b = 0, a = 1$ . Calculate

$$\left[ \int_{-\infty}^{\infty} dx e^{-x^2} \right] = \int \int dx dy e^{-(x^2+y^2)} = \int_0^{2\pi} \int_0^{\infty} dr r e^{-r^2} = 2\pi \int_0^{\infty} \frac{dx}{2} e^{-x} = \pi \quad (1.28)$$

and take the square-root of this equation. Then do the case with general  $a$  and  $b$  by completing the square in the exponential and substitution (exercise!).

### 1.3.5 Example: $\chi^2$ distribution

**Definition 3 ( $\chi^2$  Distribution).** *The function*

$$\rho(x) \equiv \frac{1}{2^{n/2} \Gamma(n/2)} x^{n/2-1} e^{-x/2} \theta(x) \quad (1.29)$$

is the probability density of the  $\chi^2$  distribution with  $n$  degrees of freedom. Here,

$$\Gamma(z) \equiv \int_0^{\infty} dx x^{z-1} e^{-x} \quad (1.30)$$

is the Gamma function and

$$\theta(x) = \begin{cases} 0, & x < 0 \\ 1, & x \geq 0 \end{cases} \quad (1.31)$$

is the unit-step (Heavyside) function.

### 1.3.6 Expectation value (mean value), mean square deviation

**Definition 4 (Expectation value).** *Let  $x$  be a random variable with probability density  $\rho(x)$ . Then,*

$$\bar{x} \equiv \langle x \rangle \equiv \int_{-\infty}^{\infty} dx \rho(x) x \quad (1.32)$$

is called expectation value (mean value) of  $x$ .

Example: Gauss distribution

$$\rho(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x_0)^2}{2\sigma^2}} \rightsquigarrow \langle x \rangle = \int_{-\infty}^{\infty} dx \rho(x) x = x_0. \quad (1.33)$$

If  $f(x)$  is a function of the random variable  $x$  (example:  $x$  is the value of a position measurement,  $f(x) = V(x)$  is the value of an external, fixed electric potential at  $x$ ;  $x$  random  $\rightsquigarrow f(x)$  random as well), we define the

**Definition 5 (Expectation value of a function).** *: The expectation value of a function  $f(x)$  is defined as*

$$\langle f \rangle := \int_{-\infty}^{\infty} dx \rho(x) f(x). \quad (1.34)$$

Note that (1.33) is a special case of (1.34) with  $f(x) = x$ . An important special case of (1.33) is the

**Definition 6 (Mean-square deviation).** *The mean-square deviation of  $x$  is defined as*

$$\langle \Delta x^2 \rangle \equiv \langle (x - \langle x \rangle)^2 \rangle. \quad (1.35)$$

Its value indicated how broadly scattered the individual realisations of  $x$  around its mean value  $\bar{x}$  are. Example: Gauss distribution

$$\rho(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}} \rightsquigarrow \langle \Delta x^2 \rangle = \int_{-\infty}^{\infty} dx \rho(x) x^2 = \sigma^2. \quad (1.36)$$

In this example, we have used the trick of *differentiation with respect to a parameter* in order to calculate the integral

$$\int_{-\infty}^{\infty} dx x^2 e^{-ax^2} = -\frac{\partial}{\partial a} \int_{-\infty}^{\infty} dx e^{-ax^2} = -\frac{\partial}{\partial a} \sqrt{\pi} a^{-1/2} = \frac{1}{2} \sqrt{\frac{\pi}{a^3}}. \quad (1.37)$$

### 1.3.7 The continuity equation

We generate one equation by multiplying the Schrödinger equation with  $\Psi^*(x, t)$ , where  $*$  means conjugate complex. We generate another equation by multiplying the (Schrödinger equation)\* with  $-\Psi(x, t)$  and add both equations. The result is

$$\begin{aligned} ih(\Psi^* \partial_t \Psi + \Psi \partial_t \Psi^*) &= -\frac{\hbar^2}{2m} [\Psi^* \partial_x^2 \Psi - \Psi \partial_x^2 \Psi^*] \\ ih \partial_t (\Psi \Psi^*) &= -\frac{\hbar^2}{2m} \partial_x [\Psi^* \partial_x \Psi - \Psi \partial_x \Psi^*]. \end{aligned} \quad (1.38)$$

This can be written in the form of a continuity equation:

$$\begin{cases} \frac{\partial}{\partial t} \rho(x, t) + \frac{\partial}{\partial x} j(x, t) = 0 \\ \rho(x, t) \equiv \Psi(x, t) \Psi^*(x, t) \\ j(x, t) \equiv -\frac{i\hbar}{2m} [\Psi(x, t)^* \frac{\partial}{\partial x} \Psi(x, t) - \Psi(x, t) \frac{\partial}{\partial x} \Psi^*(x, t)]. \end{cases} \quad (1.39)$$

You should check that beside the **probability density**  $\rho(x, t)$  also the **probability current density**  $j(x, t)$  both are real quantities. Eq. (1.39) in fact is the one-dimensional version of a **continuity equation**

$$\partial_t \rho(\mathbf{x}, t) + \text{div} \mathbf{j}(\mathbf{x}, t) = 0 \quad (1.40)$$

that appears in different areas of physics such as fluid dynamics or wave theory. We note that for simplicity up to here we have only dealt with the one-dimensional version of the Schrödinger equation which yields the one-dimensional version of the continuity equation. We integrate Eq. (1.39) from  $x = -\infty$  to  $x = \infty$  and assume that  $\Psi$  vanishes at infinity which is plausible: if  $\Psi$  is related to a probability, this probability should be zero at points of space that are inaccessible to the particles, i.e. at infinity. We obtain

$$\partial_t \int_{-\infty}^{\infty} dx \rho(x, t) = 0 \rightsquigarrow \int_{-\infty}^{\infty} dx \rho(x, t) = \text{const}. \quad (1.41)$$

The statistical interpretation of  $\Psi(x, t)$  is one of the central axioms of quantum mechanics.

## 1.4 Fourier Transforms and the Solution of the Schrödinger Equation

We had arrived at the Schrödinger equation starting from the wave packet

$$\Psi(x, t) = \int_{-\infty}^{\infty} dk a(k) e^{i(kx - \omega(k)t)}, \quad \hbar\omega(k) = E = \hbar^2 k^2 / (2m). \quad (1.42)$$

In the following, we formalize such superpositions of plane waves by introducing the concept of *Fourier integrals* and the Fourier transform of a function. The Fourier transform is a powerful tool to solve linear partial differential equations such as the Schrödinger equation for a free particle (potential  $V(x) = 0$ ).

### 1.4.1 Math: Fourier Integral

We define the decomposition into plane waves of a function  $f(x)$  of one variable  $x$  by its **Fourier transform**  $\tilde{f}(k)$ ,

$$\tilde{f}(k) := \int_{-\infty}^{\infty} dx f(x) e^{-ikx}, \quad f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \tilde{f}(k) e^{ikx}. \quad (1.43)$$

Remarks:

1. In this lecture, we define the Fourier transform with the factor  $1/2\pi$  as in (1.43). Some people define it symmetrically, i.e.  $1/\sqrt{2\pi}$  in front of  $f(x)$  and  $\tilde{f}(k)$ .
2. Remember the Minus signs in the exp functions.

We often use the Fourier transform  $\tilde{f}(\mathbf{k})$  in  $d$  dimensions for a function  $f(\mathbf{x})$ ,  $\mathbf{x} = (x_1, \dots, x_d)$ ,

$$\tilde{f}(\mathbf{k}) := \int_{-\infty}^{\infty} d\mathbf{x} f(\mathbf{x}) e^{-i\mathbf{k}\mathbf{x}}, \quad f(\mathbf{x}) = \frac{1}{(2\pi)^d} \int_{-\infty}^{\infty} d\mathbf{k} \tilde{f}(\mathbf{k}) e^{i\mathbf{k}\mathbf{x}}. \quad (1.44)$$

### 1.4.2 Math: Gauss function

The Gauss function

$$g(x) := \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}} \quad (1.45)$$

is a convenient example to discuss properties of the Fourier transform. It can be decomposed into plane waves by

$$\begin{aligned} \tilde{g}(k) &= \int_{-\infty}^{\infty} dx g(x) e^{-ikx} = e^{-\frac{1}{2}\sigma^2 k^2} \\ g(x) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{-\frac{1}{2}\sigma^2 k^2} e^{ikx} \end{aligned} \quad (1.46)$$

An important integral in this context is

$$\int_{-\infty}^{\infty} dx e^{-ax^2+bx} = \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{4a}}. \quad (1.47)$$

A very broad Gauss function  $g(x)$  with large  $\sigma$  is the result of a superposition of plane waves  $e^{ikx}$  in a very small range of  $k$ -values around  $k = 0$ : if  $\sigma$  is very large, the weights  $e^{-\frac{1}{2}\sigma^2 k^2}$  in the Fourier decomposition become very small for large  $|k|$ . Discuss the opposite case of small  $\sigma$ !

### 1.4.3 The Delta Functional ('Delta Function')

The parameter  $\sigma$  in the Gauss function determines its width. A broad wave packet in coordinate ( $x$ ) space corresponds to a narrow distribution of wave vectors  $k$ . What happens in the limit  $\sigma \rightarrow 0$ ? In coordinate space, this would correspond to an extremely sharp wave packet around  $x = 0$  that could serve as a model for a particle localized at  $x = 0$ . We define

$$\delta(x) \equiv \lim_{\sigma \rightarrow 0} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}. \quad (1.48)$$

As an ordinary function, this is a somewhat strange mathematical object because it is zero for all  $x \neq 0$ , but infinite for  $x = 0$ . However, it has the useful property that for any (reasonably well-behaving) function  $f(x)$

$$\int_{-\infty}^{\infty} dx' \delta(x - x') f(x') = \lim_{\sigma \rightarrow 0} \int_{-\infty}^{\infty} dx' f(x') \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x')^2}{2\sigma^2}} = f(x). \quad (1.49)$$

For example, multiplication of  $f(x')$  with  $\delta(x')$  and integration over the whole  $x'$ -axis gives the value of  $f$  at  $x = 0$ . Such an operation is called a **functional**, that is a mapping

$$\delta : f \rightarrow f(0) \quad (1.50)$$

that puts a whole function  $f$  to a (complex or real) number. Nevertheless, for historical reasons physicists call this object a *delta-function*. Remember that  $\delta(x)$  is only defined as in (1.49), that is by integration over a function ('test-function')  $f(x)$ .

Another very useful property is the Fourier transform of the Delta-function: We recall our definition

$$\begin{aligned} f(x) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \tilde{f}(k) e^{ikx}, \quad \tilde{f}(k) := \int_{-\infty}^{\infty} dx' f(x') e^{-ikx'} \\ \rightsquigarrow f(x) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dx' f(x') e^{-ikx'} e^{ikx} = \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ik(x-x')} f(x'). \end{aligned} \quad (1.51)$$

Now, comparing with the definition of the Delta function, Eq.(1.49), we recognise

$$\delta(x - x') = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ik(x-x')}. \quad (1.52)$$

The delta function is thus a superposition of *all* plane waves; the corresponding distribution of  $k$ -values in  $k$ -space is 'extremely broad', that is uniform from  $k = -\infty$  to  $k = +\infty$ . Note that we can also obtain the result  $\tilde{\delta}(k) = 1$  from the Fourier transform  $\tilde{g}(k)$  of the Gauss function  $g(x)$ , Eq. (1.46), in the limit  $\sigma \rightarrow 0$ .

### 1.4.4 \* Partial Differential Equations and Fourier Transform

The Schrödinger equation for a free particle,

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = -\frac{\hbar^2 \partial_x^2}{2m} \Psi(x, t), \quad \Psi(x, t=0) = \Psi_0(x) \quad (1.53)$$



can be solved by Fourier transformation:

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t} \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ikx} \tilde{\Psi}(k, t) &= -\frac{\hbar^2 \partial_x^2}{2m} \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ikx} \tilde{\Psi}(k, t) = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \frac{dk}{2\pi} k^2 e^{ikx} \tilde{\Psi}(k, t) \\
\rightsquigarrow 0 &= \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ikx} \left[ i\hbar \frac{\partial}{\partial t} \tilde{\Psi}(k, t) - \frac{\hbar^2 k^2}{2m} \tilde{\Psi}(k, t) \right] \\
\rightsquigarrow 0 &= i\hbar \frac{\partial}{\partial t} \tilde{\Psi}(k, t) - \frac{\hbar^2 k^2}{2m} \tilde{\Psi}(k, t). \tag{1.54}
\end{aligned}$$

The last equation is an **ordinary differential equation** in  $t$  that can be solved easily:

$$\begin{aligned}
0 &= i\hbar \frac{\partial}{\partial t} \tilde{\Psi}(k, t) - \frac{\hbar^2 k^2}{2m} \tilde{\Psi}(k, t) \\
\rightsquigarrow \tilde{\Psi}(k, t) &= \tilde{\Psi}(k, t=0) e^{-i\omega(k)t}, \quad \omega(k) := \frac{\hbar k^2}{2m}. \tag{1.55}
\end{aligned}$$

Here, the *initial value*  $\tilde{\Psi}(k, t=0)$  appears; it is given by our definition for the Fourier transform

$$\tilde{\Psi}(k, t=0) = \int_{-\infty}^{\infty} dx \Psi(x, t=0) e^{-ikx} = \int_{-\infty}^{\infty} dx \Psi_0(x) e^{-ikx} = \tilde{\Psi}_0(k) \tag{1.56}$$

Therefore, if we know the initial wave function  $\Psi_0(x)$ , we know its Fourier transform  $\tilde{\Psi}(k, t=0)$  and can calculate the solution  $\Psi(x, t)$  at a later time  $t > 0$  by Fourier back transformation,

$$\begin{aligned}
\Psi(x, t) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \tilde{\Psi}(k, t) e^{ikx} = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ikx} e^{-i\frac{\hbar k^2 t}{2m}} \tilde{\Psi}_0(k) \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ikx} e^{-i\omega(k)t} \int_{-\infty}^{\infty} dx' \Psi(x', t=0) e^{-ikx'} \\
&= \int_{-\infty}^{\infty} dx' \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ik(x-x') - i\omega(k)t} \Psi(x', t=0) \\
&= \int_{-\infty}^{\infty} dx' \underline{G(x, x'; t, t=0)} \Psi(x', t=0), \tag{1.57}
\end{aligned}$$

where we defined the **propagator** of the particle which propagates the wave function from its initial form at  $t=0$  to its form at a later time  $t > 0$ .

## 1.5 Position and Momentum in Quantum Mechanics

### 1.5.1 Expectation values in quantum mechanics

We had seen that the square of the wave function,  $|\Psi(x, t)|^2$ , describing a particle in a potential  $V(x)$ , is a probability density to find the particle at  $x$  at time  $t$ . The result of a single measurement of  $x$  can only be predicted to have a certain probability, but if many measurements of the position  $x$  under identical conditions are repeated, the average value (expectation value) of  $x$  is

$$\langle x \rangle_t = \int dx |\Psi(x, t)|^2 x. \tag{1.58}$$

We have again adopted a one-dimensional version for simplicity, in three dimensions the expectation value is completely analogous,

$$\langle \mathbf{x} \rangle_t = \int d^3x |\Psi(\mathbf{x}, t)|^2 \mathbf{x}. \tag{1.59}$$

Note that the expectation value is now a three-dimensional vector which is a function of time  $t$ . We have indicated the time-dependence by the notation  $\langle \dots \rangle_t$ .

Next, we would like to know the expectation value of the momentum  $\mathbf{p}$  of the particle. To determine  $\mathbf{x}$  and  $\mathbf{p}$  for a given massive object (like a planet revolving around the sun) at time  $t$  is one of the aims of classical mechanics. In quantum mechanics, we only have the probability density  $|\Psi(x, t)|^2$ , but we can calculate expectation values: We define the expectation value for the momentum  $p$  (one-dimensional version) as

$$\langle p \rangle_t \equiv m \frac{d}{dt} \langle x \rangle_t. \tag{1.60}$$

This seems plausible because in classical mechanics  $p = m\dot{x}$ . Later we will see that an equivalent definition is also possible, using the de Broglie relation  $p = \hbar k$ . We write

$$\langle p \rangle_t = m \frac{d}{dt} \langle x \rangle_t = m \int dx \frac{d}{dt} |\Psi(x, t)|^2 x = -m \int dx \frac{\partial}{\partial x} j(x, t) x. \tag{1.61}$$

Now, we re-call the definition of the current-density and the continuity equation, Eq.(1.39),

$$\begin{array}{l}
\frac{\partial}{\partial t} \rho(x, t) + \frac{\partial}{\partial x} j(x, t) = 0 \\
\rho(x, t) \equiv \Psi(x, t) \Psi^*(x, t) \\
j(x, t) \equiv -\frac{i\hbar}{2m} \left[ \Psi(x, t)^* \frac{\partial}{\partial x} \Psi(x, t) - \Psi(x, t) \frac{\partial}{\partial x} \Psi^*(x, t) \right].
\end{array}$$

We therefore find

$$\begin{aligned}
\langle p \rangle_t &= [\text{partial integration}] = m \int dx j(x, t) = [\text{definition of } j] \\
&= -\frac{i\hbar}{2} \int dx [\Psi^*(x, t) \partial_x \Psi(x, t) - \Psi(x, t) \partial_x \Psi^*(x, t)] = [\text{partial integration}] \\
&= -\frac{i\hbar}{2} \int dx [\Psi^*(x, t) \partial_x \Psi(x, t) + \partial_x \Psi(x, t) \Psi^*(x, t)] \\
&= \int dx [\Psi^*(x, t) \frac{\hbar \partial_x}{i} \Psi(x, t)]. \tag{1.62}
\end{aligned}$$

We compare

$$\langle x \rangle_t = \int dx \Psi^*(x, t) x \Psi(x, t), \quad \langle p \rangle_t = \int dx \Psi^*(x, t) \frac{\hbar \partial_x}{i} \Psi(x, t) \tag{1.63}$$

and recognize that the position  $x$  corresponds to the (somewhat trivial) **operator** ‘multiplication with  $x$ ’. On the other hand, the momentum corresponds to the completely non-trivial operator  $-i\hbar \partial_x$ . A similar calculation leads to

$$\langle x^2 \rangle_t = \int dx \Psi^*(x, t) x^2 \Psi(x, t), \quad \langle p^2 \rangle_t = \int dx \Psi^*(x, t) \left[ \frac{\hbar \partial_x}{i} \right]^2 \Psi(x, t). \tag{1.64}$$

Again, the above can easily be generalized to three dimensions when  $x \rightarrow \mathbf{x}$  and  $\partial_x \rightarrow (\partial_x, \partial_y, \partial_z) = \nabla$  (gradient or Nabla-operator).

**Axiom 2:** Expectation values of functions  $F(\mathbf{x})$  of the position or  $G(\mathbf{p})$  of the momentum for a quantum mechanical system described by a wave function  $\Psi(\mathbf{x}, t)$  are calculated as

$$\begin{aligned}\langle F(\mathbf{x}) \rangle_t &= \int d^3x \Psi^*(\mathbf{x}, t) F(\mathbf{x}) \Psi(\mathbf{x}, t) \\ \langle G(\mathbf{p}) \rangle_t &= \int d^3x \Psi^*(\mathbf{x}, t) G\left(\frac{\hbar \nabla}{i}\right) \Psi(\mathbf{x}, t).\end{aligned}\quad (1.65)$$

The position  $\mathbf{x}$  corresponds to the operator ‘multiplication with  $\mathbf{x}$ ’, the momentum  $\mathbf{p}$  to the operator  $-i\hbar\nabla$ , applied to the wave function as in (1.63),(1.64),(1.65).

This correspondence in particular holds for the total energy, which in classical mechanics for a conservative system (energy is conserved) is given by a **Hamilton function**

$$H(\mathbf{p}, \mathbf{x}) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}). \quad (1.66)$$

The **correspondence principle** from axiom 2 tells us that this Hamilton function in quantum mechanics has to be replaced by a **Hamilton operator (Hamiltonian)**  $\hat{H}$

$$\hat{H} = -\frac{\hbar^2 \Delta}{2m} + V(\hat{\mathbf{x}}). \quad (1.67)$$

Here, we have used the definition of the Laplace operator  $\Delta = \nabla \cdot \nabla$ . In Cartesian coordinates, it is  $\Delta = \partial_x^2 + \partial_y^2 + \partial_z^2$ . The Hamilton operator represents the total energy of the particle with mass  $m$  in the potential  $V(\mathbf{x})$ . We have introduced the hat as a notation for operators, but often the hat is omitted for simplicity. We make the important observation that  $\hat{H}$  is exactly the expression that appears on the right hand side of the Schrödinger equation (1.21). This means we can write the Schrödinger equation as

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{x}, t) = \hat{H} \Psi(\mathbf{x}, t). \quad (1.68)$$

This is the most general form of the Schrödinger equation in quantum mechanics. The replacement of  $\mathbf{x}$  and  $\mathbf{p}$  in quantum mechanics is

**Axiom 3:** The position  $\mathbf{x}$  and momentum  $\mathbf{p}$  are **operators** acting on wave functions,

$$\mathbf{x} \rightarrow \hat{\mathbf{x}}, \quad \mathbf{p} \rightarrow \frac{\hbar}{i} \nabla. \quad (1.69)$$

### 1.5.2 Example: Wave packet

We consider the wave function (wave packet, see above)

$$\Psi(x) = \frac{1}{\sqrt{\sqrt{\pi} a^2}} \exp\left(-\frac{x^2}{2a^2}\right). \quad (1.70)$$

1. We calculate

$$\langle x \rangle = \int_{-\infty}^{\infty} dx \Psi^*(x, t) x \Psi(x, t) = 0, \quad \langle p \rangle = \int_{-\infty}^{\infty} dx \Psi^*(x, t) \frac{\hbar \partial_x}{i} \Psi(x, t) = 0. \quad (1.71)$$

2. We calculate (see problem sheet 1)

$$\langle p^2 \rangle = \frac{\hbar^2}{2a^2}, \quad \langle x^2 \rangle = \frac{a^2}{2}. \quad (1.72)$$

By this we obtain for the **mean square deviations** of the position  $x$  and the momentum  $p$ ,

$$\Delta p^2 = \langle p^2 \rangle - \langle p \rangle^2 = \langle p^2 \rangle = \frac{\hbar^2}{2a^2}, \quad \Delta x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \langle x^2 \rangle = \frac{a^2}{2}.$$

The product of the two is just

$$\Delta x^2 \cdot \Delta p^2 = \frac{\hbar^2}{4}.$$

The particular case of our wave packet fulfills the **Heisenberg uncertainty relation**

$$\Delta x^2 \cdot \Delta p^2 \geq \frac{\hbar^2}{4}. \quad (1.73)$$

with the =-sign. We will later prove that there are Heisenberg uncertainty relations for arbitrary pairs of operators and not only for  $x$  and  $p$ .

### 1.5.3 The commutator $[x, p]$

Position  $x$  and momentum  $p$  are operators in quantum mechanics. Acting on wave functions, the operator product  $xp$  has the property

$$\begin{aligned}\hat{x}\hat{p}\Psi(x) &= \frac{\hbar}{i} x \frac{\partial}{\partial x} \Psi(x) = \frac{\hbar}{i} x \Psi'(x) \\ \hat{p}\hat{x}\Psi(x) &= \frac{\hbar}{i} \frac{\partial}{\partial x} x \Psi(x) = \frac{\hbar}{i} (\Psi(x) + x \Psi'(x))\end{aligned}\quad (1.74)$$

The result depends on the order of  $\hat{x}$  and  $\hat{p}$ : both operators do not commute. One has

$$(\hat{x}\hat{p} - \hat{p}\hat{x})\Psi(x) = i\hbar\Psi(x) \quad (1.75)$$

Comparing both sides, we have the **commutation relation**

$$[\hat{x}, \hat{p}] := \hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar. \quad (1.76)$$

Here, we have defined the **commutator**  $[A, B] := AB - BA$  of two operators  $A$  and  $B$ . Generalized to three dimensions with the three components  $\hat{x}_k$  of  $\hat{\mathbf{x}}$  and  $\hat{p}_k$  of  $\hat{\mathbf{p}}$ ,  $k = 1, 2, 3$ , one has the **canonical commutation relations**

$$\begin{aligned}[\hat{x}_k, \hat{p}_l] &= i\hbar \delta_{kl} \\ \delta_{kl} &:= 1, \quad k = l, \quad \text{and } 0 \text{ else.}\end{aligned}\quad (1.77)$$

## 2. WAVE MECHANICS

### 2.1 The Stationary Schrödinger Equation

Much of what we will be concerned with in this lecture are the solutions of the Schrödinger equation for a particle of mass  $m$  in a potential  $V(\mathbf{x})$ ,

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{x}, t) = \left[ -\frac{\hbar^2 \Delta}{2m} + V(\mathbf{x}) \right] \Psi(\mathbf{x}, t) \equiv \hat{H} \Psi(\mathbf{x}, t). \quad (2.1)$$

Like Newton's laws in classical mechanics, the Schrödinger equation is so important that generation of physicists have worked out how to solve it for physically interesting cases. Unfortunately, in general (i.e. for a general form of the potential  $V(\mathbf{x})$ ) the Schrödinger equation is not exactly soluble, and one has to retreat to approximate methods. There are, however, important classes of solutions that can be obtained exactly, most of which were 'milestones' in the development of the theory. Among them are the hydrogen atom, the harmonic oscillator, or one-dimensional problems which we will discuss in this chapter.

#### 2.1.1 Stationary states

The Schrödinger equation is a partial differential equation: we have one partial derivative with respect of time  $t$  and the Laplace operator  $\Delta$  which is a differential operator,  $\Delta = \partial_x^2 + \partial_y^2 + \partial_z^2$  in three dimensions and rectangular coordinates.

**Step 1:** To solve (2.1), we make the separation ansatz

$$\Psi(\mathbf{x}, t) = \psi(\mathbf{x})f(t). \quad (2.2)$$

Inserting into (2.1) we have

$$\frac{i\hbar \partial_t f(t)}{f(t)} = \frac{\hat{H} \psi(\mathbf{x})}{\psi(\mathbf{x})} = E, \quad (2.3)$$

where we have separated the  $t$ - and the  $\mathbf{x}$ -dependence. Both sides of (2.3) depend on  $t$  resp.  $\mathbf{x}$  independently and therefore must be constant  $= E$ . Solving the equation for  $f(t)$  yields  $f(t) = \exp[-iEt/\hbar]$  and therefore

$$\Psi(\mathbf{x}, t) = \psi(\mathbf{x})e^{-iEt/\hbar}. \quad (2.4)$$

We recognize: the time evolution of the wave function  $\Psi(\mathbf{x}, t)$  is solely determined by the factor  $\exp[-iEt/\hbar]$ . Furthermore, the constant  $E$  must be an energy (dimension!).

**Step 2:** To determine  $\psi(\mathbf{x})$ , we have to solve the **stationary Schrödinger equation**

$$\hat{H} \psi(\mathbf{x}) = E \psi(\mathbf{x}) \iff \left[ -\frac{\hbar^2 \Delta}{2m} + V(\mathbf{x}) \right] \psi(\mathbf{x}) = E \psi(\mathbf{x}). \quad (2.5)$$

Mathematically, the equation  $\hat{H} \psi = E \psi$  with the operator  $\hat{H}$  is an **eigenvalue equation**. We know eigenvalue equations from linear algebra where  $\hat{H}$  is a matrix and  $\psi$  is a vector. The time-independent wave functions  $\psi(\mathbf{x})$  are called stationary wave functions or **stationary states**. We will see in the following that in general, solutions of the stationary Schrödinger equation do not exist for arbitrary  $E$ . Rather, many potentials  $V(\mathbf{x})$  give rise to solutions only for certain discrete values of  $E$ , the eigenvalues of the stationary Schrödinger equation, and the possible energy values become quantized.

#### 2.1.2 Math Revision: Eigenvalues of a Two-by-Two-Matrix

An example we will need later is a 2 by 2 matrix eigenvalue problem

$$\hat{A} \underline{\phi} = \lambda \underline{\phi}, \quad \hat{A} = \begin{pmatrix} a & b \\ b^* & c \end{pmatrix}. \quad (2.6)$$

The eigenvalues are obtained from

$$\begin{aligned} (\hat{A} - \lambda \hat{1}) \underline{\phi} &= \underline{0} \rightsquigarrow \det(\hat{A} - \lambda \hat{1}) = 0 \\ \rightsquigarrow \begin{vmatrix} a - \lambda & b \\ b^* & c - \lambda \end{vmatrix} &= 0 \rightsquigarrow (a - \lambda)(c - \lambda) - |b|^2 = 0 \\ &\rightsquigarrow \lambda^2 - (a + c)\lambda + ac - |b|^2 = 0 \\ \lambda_{\pm} &= \frac{a + c}{2} \pm \sqrt{\frac{(a - c)^2}{4} + |b|^2}. \end{aligned} \quad (2.7)$$

Revision: Check how to calculate the corresponding eigenvectors!

#### 2.1.3 Stationary States in One Dimension

In this section, we study the stationary Schrödinger equation for an important class of potentials  $V(\mathbf{x}) = V(x)$  that only depend on one spatial coordinate  $x$  and are independent of  $y$  and  $z$ . Such potentials could be generated, for example, by electric fields that only vary in one direction  $x$  of space and are constant in the other directions.

We make a separation ansatz for  $\psi(\mathbf{x})$ ,

$$\psi(\mathbf{x}) = \phi(x)e^{i(k_y y + k_z z)}. \quad (2.8)$$

Inserting into the stationary Schrödinger equation yields

$$\begin{aligned} \left[ -\frac{\hbar^2 \Delta}{2m} + V(x) \right] \psi(\mathbf{x}) &= E \psi(\mathbf{x}) \\ \left[ -\frac{\hbar^2 \partial_x^2}{2m} + \frac{\hbar^2}{2m}(k_y^2 + k_z^2) + V(x) \right] \phi(x)e^{i(k_y y + k_z z)} &= E \phi(x)e^{i(k_y y + k_z z)} \\ \left[ -\frac{\hbar^2 \partial_x^2}{2m} + V(x) \right] \phi(x) &= \tilde{E} \phi(x) \\ \tilde{E} &:= E - \frac{\hbar^2}{2m}(k_y^2 + k_z^2). \end{aligned} \quad (2.9)$$

The general solution therefore can be written as the product of **two plane waves** running in the  $y - z$ -plane, and a wave function  $\phi(x)$  which is the solution of (2.9). This means we

have just to solve the one-dimensional stationary Schrödinger equation, with the energy  $E$  replaced by  $E - \hbar^2/2m(k_y^2 + k_z^2)$  which is the energy for the one-dimensional motion in the  $x$ -direction. Together with  $\hbar^2/2m(k_y^2 + k_z^2)$ , the kinetic energy of the motion in the  $y$ - $z$ -plane, this is just the total energy  $E$ . With the potential  $V(\mathbf{x}) = V(x)$ , the particle sees no potential change when moving in only  $y$ - or  $z$ -direction: there is no force acting on the particle in this direction which is why its free motion turns out to be described by plane waves in the  $y$ - and  $z$ -direction.

In the following, we will therefore only consider the rest of the problem, i.e. the motion in  $x$ -direction.

### 2.1.4 Piecewise Constant one-Dimensional Potentials

We consider the one-dimensional stationary Schrödinger equation

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E\psi(x), \quad (2.10)$$

where for the sake of a nicer notation we again write  $E$  instead of  $\tilde{E}$  and  $\psi(x)$  instead of  $\phi(x)$ . Furthermore, there is only one variable  $x$  so that the partial derivative  $\partial_x = d/dx$ .

In the following, we will concentrate on the important case where  $V(x)$  is piecewise constant, i.e.

$$V(x) = \begin{cases} V_1, & -\infty < x \leq x_1 \\ V_2, & x_1 < x \leq x_2 \\ \dots & \dots \\ V_N, & x_{N-1} < x \leq x_N \\ V_{N+1}, & x_N < x < \infty \end{cases} \quad (2.11)$$

Let us look at (2.10) on an interval where  $V(x)$  is constant, say  $[x_1, x_2]$  with  $V = V_2$ . The Schrödinger equation

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V \right] \psi(x) = E\psi(x) \quad (2.12)$$

on this interval is a second order ordinary differential equation with constant coefficients. There are **two independent solutions**

$$\psi_+(x) = e^{ikx}, \quad \psi_-(x) = e^{-ikx}, \quad k := \sqrt{\frac{2m}{\hbar^2}(E - V)}. \quad (2.13)$$

1. If  $E > V$ , the **wave vector**  $k$  is a real quantity and the two solutions  $\psi_{\pm}(x)$  are plane waves running in the positive and the negative  $x$ -direction. Such solutions are called oscillatory solutions.
2. If  $E < V$ ,  $k$  becomes imaginary and we write

$$k = i\kappa := i\sqrt{\frac{2m}{\hbar^2}(V - E)} \quad (2.14)$$

with the real quantity  $\kappa$ . The two independent solutions then become exponential functions  $e^{\pm\kappa x}$ . Such solutions are called exponential solutions.

For fixed energy  $E$ , the general solution  $\psi(x)$  will be a **superposition**, that is a linear combination

$$\psi(x) = ae^{ikx} + be^{-ikx} \quad (2.15)$$

with  $k$  either real or imaginary,  $k = i\kappa$ . Since the wave function in general is a complex function, the coefficients  $a, b$  can be complex numbers. Note that we can not have linear combinations with one real and one imaginary term in the exponential like  $ae^{ikx} + be^{-\kappa x}$ ,  $a, b \neq 0$ .

The solution of our Schrödinger equation with the piece-wise constant potential (2.11) must fulfill it everywhere on the  $x$ -axis. Therefore, it can be written as

$$\psi(x) = \begin{cases} a_1 e^{ik_1 x} + b_1 e^{-ik_1 x}, & -\infty < x \leq x_1 \\ a_2 e^{ik_2 x} + b_2 e^{-ik_2 x}, & x_1 < x \leq x_2 \\ \dots & \dots \\ a_N e^{ik_N x} + b_N e^{-ik_N x}, & x_{N-1} < x \leq x_N \\ a_{N+1} e^{ik_{N+1} x} + b_{N+1} e^{-ik_{N+1} x}, & x_N < x < \infty \end{cases} \quad (2.16)$$

with complex constants  $a_j, b_j$  and  $k_j = \sqrt{(2m/\hbar^2)(E - V_j)}$  either real or complex.

## 2.2 The Infinite Potential Well

### 2.2.1 Wave functions and eigenenergies

We first study the case where the motion of the particle is restricted within the interval  $[x_1, x_2] = [0, L]$ ,  $L > 0$  between the infinitely high walls of the potential

$$V(x) = \begin{cases} \infty, & -\infty < x \leq 0 \\ 0, & 0 < x \leq L \\ \infty, & L < x < \infty \end{cases} \quad (2.17)$$

Outside the interval  $[0, L]$  the particle can not exist and its wave function must be zero, i.e.

$$\psi(x) = \begin{cases} 0, & -\infty < x \leq 0 \\ ae^{ikx} + be^{-ikx}, & 0 < x \leq L \\ 0, & L < x < \infty \end{cases} \quad (2.18)$$

1. We demand that the wave function vanishes at  $x = 0$  and  $x = L$  so that it is continuous at these points. Clearly, this makes physically sense because at  $x = 0, L$  the potential is infinitely high and the probability density  $|\psi(x)|^2$  to find the particle there should be zero. We obtain

$$\begin{aligned} \psi(0) &= 0 \rightsquigarrow 0 = a + b \rightsquigarrow \psi(x) = c \sin(kx), \quad 0 \leq x \leq L, \quad c = \text{const.} \\ \psi(L) &= 0 \rightsquigarrow \sin(kL) = 0. \end{aligned} \quad (2.19)$$

The first condition tells us that the wave function must be a sine-function. The second condition is more interesting: it sets a condition for the possible values  $k_n$  that  $k$  can have,

$$kL = n\pi \rightsquigarrow k \equiv k_n = \frac{n\pi}{L}, \quad n = 1, 2, 3, \dots \quad (2.20)$$

The second **boundary condition** at  $x = L$  restricts the possible values of the energy  $E$ , because  $k := \sqrt{(2m/\hbar^2)(E - V)} = \sqrt{(2m/\hbar^2)E}$ . Therefore, the energy can only acquire values

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \hbar^2 \pi^2}{2mL^2}, \quad n = 1, 2, 3, \dots \quad (2.21)$$

This is the first case where we encounter a **quantisation of energy**. The reason for the quantization here is obvious: the wave functions  $\psi(x)$  have to ‘fit’ into the well, similar to classical waves in a resonator which only allows waves with certain wave lengths. The allowed wave vectors  $k_n$  then are related to the energy by the de Broglie relation  $p = \hbar k \rightsquigarrow p_n = \hbar k_n$ , and the energy within the well is just the kinetic energy  $E = p^2/2m$  (since the potential is zero there) whence (2.21) follows.

2. The potential well gives only rise to discrete values of the energy. One says that the **spectrum of energies is discrete**. If we did not have the confinement potential, the wave functions would just be plane waves  $e^{\pm ikx}$  with arbitrary values  $k$  and therefore arbitrary, continuous values for the energies  $E = \hbar^2 k^2/2m$ . In such a case the spectrum is called a **continuous spectrum**.

3. In order to interpret the absolute square wave of the wave functions  $\psi_n(x) = c \sin(k_n x)$  as a probability density, we have to demand

$$\begin{aligned} 1 &= \int_0^L dx |\psi_n(x)|^2 = \int_0^L dx |c|^2 \sin^2(n\pi x/L) \\ &= \frac{1}{2} \int_0^L dx |c|^2 [1 - \cos(2n\pi x/L)] = \frac{|c|^2 L}{2} \\ |c|^2 &= \frac{2}{L} \rightsquigarrow c = \sqrt{\frac{2}{L}} e^{i\varphi} \rightsquigarrow \psi_n(x) = \sqrt{\frac{2}{L}} \sin(n\pi x/L) e^{i\varphi}, \end{aligned} \quad (2.22)$$

where  $\varphi \in R$  is a (real) phase factor. This **normalization condition** determines the wave functions  $\psi_n(x)$  uniquely only up to a **phase factor**: if  $\Psi$  is a normalized solution of the Schrödinger equation, so is  $\Psi e^{i\varphi}$ , i.e. the same wave function multiplied with a constant overall phase factor. Usually, we do not distinguish between such wave functions since they describe the same **state** of the particle, and one says that the state is only determined ‘up to a phase’ which is irrelevant when calculating, for example, the probability density  $|\Psi|^2$  or expectation values.

This is different, however, for superpositions of two different wave functions, where the *relative* phase difference is important and leads, for example, to interference.

### 2.2.2 The Hilbert space $\mathcal{H}$ of wave functions

We have seen that the wave functions with fixed energy  $E$  of a particle of mass  $m$  in an infinitely high potential well of width  $L$  are given by

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad E = E_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2}, \quad n = 1, 2, 3, \dots \quad (2.23)$$

1. We have omitted the arbitrary phase factor  $e^{i\varphi}$  here as discussed above.
2. The index  $n$  is called **quantum number**, it labels the possible solutions of the stationary Schrödinger equation

$$\hat{H}\psi_n(x) = E_n \psi_n(x). \quad (2.24)$$

As in linear algebra, the  $E_n$  are called **eigenvalues** (eigenvalues of the energy) and the  $\psi_n(x)$  are called **eigenvectors** (eigenfunctions) of the Hamiltonian  $\hat{H}$ .

3. We only have positive integers  $n$ : negative integers  $-|n|$  would lead to solutions  $\psi_{-|n|}(x) = -\psi_n(x)$  which are just the negative of the wave functions with positive  $n$ . They describe the

same state of the particle which is unique up to a phase  $e^{i\varphi}$  (for example  $e^{i\varphi} = -1$ ) anyway.  $\psi_{-|n|}(x)$  is **linear dependent** on  $\psi_n(x)$ .

4. The eigenvectors of  $\hat{H}$ , i.e. the functions  $\psi_n(x)$ , form the basis of a **linear vector space**  $\mathcal{H}$  of functions  $f(x)$  defined on the interval  $[0, L]$  with  $f(0) = f(L) = 0$ . The  $\psi_n(x)$  form an orthonormal basis:

$$\int_0^L dx |\psi_n(x)|^2 = 1, \quad \int_0^L dx \psi_n^*(x) \psi_m(x) = \delta_{nm}. \quad (2.25)$$

(We can omit the  $*$  here because the  $\psi_n$  are real). Note that the orthonormal basis is of infinite dimension because there are infinitely many  $n$ . The infinite dimension of the vector space (function space)  $\mathcal{H}$  is the main difference to ordinary, finite dimensional vector spaces like the  $R^3$ .

5. Any wave function  $\psi(x) \in \mathcal{H}$  (like any arbitrary vector in, e.g., the vector space  $R^3$ ) can be expanded into a linear combination of basis ‘vectors’, i.e. eigenfunctions  $\psi_n(x)$ :

$$\psi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x), \quad c_n = \int_0^L dx \psi(x) \psi_n(x). \quad (2.26)$$

A vector space with these properties is called a **Hilbert space**. The Hilbert space is the central mathematical object of quantum theory.

Example	vectors and matrices	Particle in Quantum Well
vector	$\mathbf{x}$	wave function $\psi(x)$
space	vector space	Hilbert space
linear operator	matrix $A = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	Hamiltonian $H_{\text{well}}$
eigenvalue problem	$A\mathbf{x} = \lambda\mathbf{x}$	$H_{\text{well}}\psi_n = E_n\psi_n$
eigenvalue	$\lambda_1 = 1, \lambda_2 = -1$	$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, n = 1, 2, 3, \dots$
eigenvector	$\mathbf{x}_{1,2} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$	wave function $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$
scalar product	$\langle \mathbf{x}   \mathbf{y} \rangle \equiv \sum_{n=1}^2 x_n^* y_n$	$\langle \psi   \phi \rangle \equiv \int_0^L dx \psi^*(x) \phi(x)$
orthogonal basis	$\langle \mathbf{e}_n   \mathbf{e}_m \rangle = \delta_{nm}$	$\langle \psi_n   \psi_m \rangle = \delta_{nm}$
dimension	2	$\infty$
completeness	$\mathbf{x} = \sum_{n=1}^2 (\mathbf{e}_n   \mathbf{x}) \mathbf{e}_n$	$\psi = \sum_{n=1}^{\infty} \langle \psi_n   \psi \rangle \psi_n$
vector components	$\mathbf{x} = (\langle \mathbf{e}_1   \mathbf{x} \rangle, \langle \mathbf{e}_2   \mathbf{x} \rangle)$	$\psi = (\langle \psi_1   \psi \rangle, \langle \psi_2   \psi \rangle, \dots)$

We will explain this table in greater detail in the next chapter where we turn to the foundations of quantum mechanics.

## 2.3 The Potential Well

### 2.3.1 Wave functions and energy eigenvalues for $E < 0$

Our second one-dimensional problem is the motion of a particle in a potential well of finite depth  $V$  and width  $2a > 0$ , i.e. a potential

$$V(x) = \begin{cases} 0, & -\infty < x \leq -a \\ -V < 0, & -a < x \leq a \\ 0 & a < x < \infty \end{cases} \quad (2.27)$$

According to our general equation, the wave functions for energies  $-|V| < E = -|E| < 0$  must have the form

$$\psi(x) = \begin{cases} a_1 e^{\kappa x} + b_1 e^{-\kappa x}, & -\infty < x \leq -a \\ a_2 e^{ikx} + b_2 e^{-ikx}, & -a < x \leq a \\ a_3 e^{\kappa x} + b_3 e^{-\kappa x}, & a < x < \infty \end{cases} \quad (2.28)$$

where

$$k = \sqrt{(2m/\hbar^2)(-|E| + V)}, \quad \kappa = \sqrt{(2m/\hbar^2)|E|}. \quad (2.29)$$

The wave function has to vanish for  $x \rightarrow \pm\infty$  which can only be fulfilled if  $b_1 = a_3 = 0$ .

### 2.3.2 The parity

For **symmetric potentials**  $V(x) = V(-x)$ , the Schrödinger equation has an important property: If  $\psi(x)$  is a solution of  $\hat{H}\psi(x) = E\psi(x)$ , then also  $\psi(-x)$  is a solution with the same  $E$ , i.e.  $\hat{H}\psi(-x) = E\psi(-x)$  (replace  $-x \rightarrow x$  and note that  $\partial_x^2 = \partial_{-x}^2$ ). Since  $\hat{H}$  is linear, also linear combinations of solutions with the same eigenvalue  $E$  are solutions with eigenvalue  $E$ , in particular the symmetric (even) and anti symmetric (odd) linear combinations

$$\psi_e(x) := \frac{1}{\sqrt{2}}[\psi(x) + \psi(-x)], \quad \psi_o(x) := \frac{1}{\sqrt{2}}[\psi(x) - \psi(-x)]. \quad (2.30)$$

These are the solutions with even (e) and odd (o) parity, respectively.

### 2.3.3 Even and odd solutions for the potential well

Applied to our potential well, we can classify the solutions into even and odd,

$$\psi_e(x) = \begin{cases} a_1 e^{\kappa x}, \\ a_2 \cos(kx), \\ a_1 e^{-\kappa x}, \end{cases} \quad \psi_o(x) = \begin{cases} -A_1 e^{\kappa x}, & -\infty < x \leq -a \\ A_2 \sin(kx), & -a < x \leq a \\ A_1 e^{-\kappa x}, & a < x < \infty \end{cases} \quad (2.31)$$

The wave function  $\psi(x)$  and its derivative  $\psi'(x)$  have to be continuous at  $x = \pm a$ . Therefore, also the **logarithmic derivative**

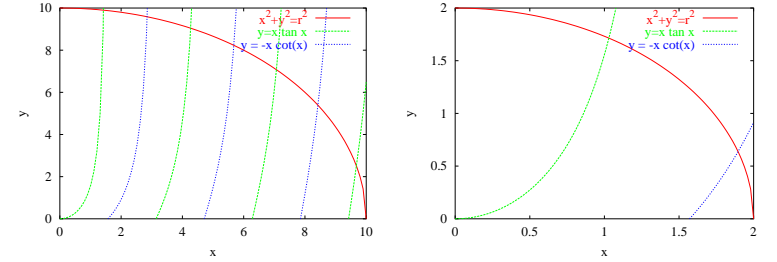
$$\frac{\psi'(x)}{\psi(x)} = \frac{d}{dx} \log \psi(x) \quad (2.32)$$

has to be continuous. This is a convenient way to obtain an equation that relates  $k$  and  $\kappa$  and determines the possible energy values: we calculate the logarithmic derivative for  $x = a \pm \varepsilon$ ,  $\varepsilon \rightarrow 0$  which yields

$$\begin{aligned} -\kappa &= -k \tan(ka), & \text{even solution} \\ -\kappa &= k \cot(ka), & \text{odd solution} \\ k &= \sqrt{(2m/\hbar^2)(-|E| + V)}, & \kappa = \sqrt{(2m/\hbar^2)|E|}. \end{aligned} \quad (2.33)$$

These are **transcendent equations** for the energy  $E$ : we introduce auxiliary dimensionless variables

$$x \equiv ka, \quad y = \kappa a \rightsquigarrow x^2 + y^2 = r^2 \equiv \frac{2ma^2V}{\hbar^2}, \quad V > 0. \quad (2.34)$$



**Fig. 2.1:** Graphical solution of (2.35) for  $r = 10$  (left) and  $r = 2$  (right).

The equations

$$\begin{aligned} y &= x \tan x, & x^2 + y^2 = r^2 & \text{even solution} \\ y &= -x \cot x, & x^2 + y^2 = r^2 & \text{odd solution} \end{aligned} \quad (2.35)$$

describe two curves in the  $x$ - $y$ -plane, i.e. the circle  $x^2 + y^2 = r^2$ , with

$$r \equiv \sqrt{\frac{2m}{\hbar^2} a^2 V}, \quad (2.36)$$

and the curve  $y = x \tan(x)$  ( $y = -x \cot(x)$  for the odd solution), whose intersections determine a fixed number of points  $(x_n, y_n)$  in the quadrant of positive  $x$  and  $y$ . These determine the energy eigenvalues  $E_n$  via the definition of  $k$  and  $\kappa$ . Of course, the  $E_n$  depend on the value of the parameter  $r$  which in turn is determined by the depth of the potential well  $V$ , its width  $a$  and the particle mass  $m$ .

To obtain precise values for the possible energy eigenvalue  $E_n$ , one has to numerically solve (2.35). A convenient method to obtain a qualitative picture, however, is the graphical solution of the transcendental equations as shown in Fig. (2.1). The intersections  $y_n$ ,  $n = 1, 2, \dots$  of the  $x \tan(x)$ - or  $-x \cot(x)$ -curves with the circle of radius  $r$  determine  $E_n$  via  $E_n = -(\hbar^2/2ma^2)y_n^2$  (remember that we have required  $E_n < 0$ )

1. There are only a finite number  $N$  of solutions for the energies  $E_1 < E_2 < \dots < E_N$  depending on the value of the parameter  $r$ .
2. The wave function corresponding to the lowest eigenvalue  $E_1$  is even. Even and odd solutions alternate when 'climbing up' the ladder of possible eigenvalues  $E_n$ .

## 2.4 Scattering states in one dimension

In the above discussion of the finite depth potential well, we had so far only considered wave functions with energy  $E < 0$ . They gave rise to a **discrete spectrum of energies** with states that are **localized** within the potential well, that is outside the well the wave functions decay exponentially. This means that the probability to find the particle outside the well is exponentially small, i.e. the particle is bound to the potential well. The corresponding wave functions are therefore called **bound states**. Also in the example of the infinitely high potential well, we only had bound states because the particle was restricted within the well.

What about wave functions of the finite depth potential well with positive energies  $E$ ? The discussion of these states leads us to the concept of **scattering** states with continuous arbitrary energies  $E$  (**continuous spectrum**). Furthermore, we will find the **tunnel effect** which is an important quantum mechanical phenomenon. We discuss it first again within our general scheme of piecewise constant potentials.

#### 2.4.1 Plane waves

The simplest case is the one where the potential  $V(x)$  is zero throughout: the two independent solutions of the Schrödinger equation then are **plane waves**

$$-\frac{\hbar^2 \partial_x^2}{2m} \psi(x) = E\psi(x) \rightsquigarrow \psi_+(x) = e^{ikx}, \quad \psi_-(x) = e^{-ikx}, \quad k = \sqrt{(2m/\hbar^2)E} \quad (2.37)$$

with positive energy  $E > 0$ . We denote both solutions as  $\psi_k(x) = e^{ikx}$  with  $k$  either positive or negative. They are **plane waves** with fixed wave vector  $k$  and therefore fixed momentum  $p = \hbar k$ . We can have no physically meaningful solutions with negative energy  $E < 0$  because in this case the wave function would become infinite either for  $x \rightarrow \infty$  or  $x \rightarrow -\infty$ .

A problem arises, however, because  $\psi_k(x)$  can not be normalized over the whole  $x$ -axis according to

$$\int_{-\infty}^{\infty} dx |\psi_k(x)|^2 = 1, \quad (2.38)$$

because this integral is infinite: the probability density, i.e. the square  $|\psi_k(x)|^2$  is constant, i.e. 1 everywhere.

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In particular, we have for the mean square deviation of the momentum and the position

$$\begin{aligned} \langle \Delta p^2 \rangle &= \lim_{L \rightarrow \infty} \left( \frac{\int_{-L/2}^{L/2} |a|^2 e^{-ikx} (-i\hbar \partial_x)^2 e^{ikx}}{\int_{-L/2}^{L/2} dx |a|^2} - \left[ \frac{\int_{-L/2}^{L/2} |a|^2 e^{-ikx} (-i\hbar \partial_x) e^{ikx}}{\int_{-L/2}^{L/2} dx |a|^2} \right]^2 \right) \\ &= \hbar^2 k^2 - \hbar^2 k^2 = 0 \\ \langle \Delta x^2 \rangle &= \lim_{L \rightarrow \infty} \left( \frac{\int_{-L/2}^{L/2} |a|^2 e^{-ikx} x^2 e^{ikx}}{\int_{-L/2}^{L/2} dx |a|^2} - \left[ \frac{\int_{-L/2}^{L/2} |a|^2 e^{-ikx} x e^{ikx}}{\int_{-L/2}^{L/2} dx |a|^2} \right]^2 \right) \\ &= \infty. \end{aligned} \quad (2.39)$$

There is no uncertainty in the momentum of the particle, but there is maximum uncertainty in its position: the wave function  $\psi_k(x)$  describes a particle with fixed momentum  $p = \hbar k$  which is completely delocalized (spread) over the  $x$ -axis.

---

A practical solution is to consider a large, but finite interval  $[-L/2, L/2]$  instead of the total  $x$ -axis, and to normalize the wave functions according to

$$\psi_k = \frac{1}{\sqrt{L}} e^{ikx}, \quad \int_{-L/2}^{L/2} dx |\psi_k(x)|^2 = 1. \quad (2.40)$$

Then, the **boundary conditions** at  $x = \pm L/2$  have to be specified. Again, a convenient (but not necessary the only) choice are **periodic boundary conditions**: we bend the interval

$[L/2, L/2]$  into a ring such that the points  $\pm L/2$  coincide. Demanding continuity of  $\psi_k$ , i.e.  $\psi_k(L/2) = \psi_k(-L/2)$ , we obtain a quantization condition for the possible  $k$ -values,

$$1 = e^{ikL} \rightsquigarrow k_n = \frac{2\pi n}{L}, \quad n = 0, \pm 1, \pm 2, \dots, \quad (2.41)$$

i.e. a discrete set of possible  $k$  values and therewith discrete energies  $E(k) = \hbar^2 k^2 / 2m$ . To each energy  $E = E_n > 0$  there are two linearly independent plane waves with wave vectors  $2\pi n/L$  and  $-2\pi n/L$ . One says the energy value  $E_n$  is **two-fold degenerate**. If  $L$  is very large, the possible values for  $k$  are still discrete but subsequent  $k$ -values get very close to each other.

#### 2.4.2 Potential scattering

We now consider a piecewise constant potential  $V(x)$  with the corresponding wave function given by

$$V(x) = \begin{cases} V_1, \\ V_2, \\ V_3, \\ \dots \\ V_N \\ V_{N+1} \end{cases} \dots \quad \psi(x) = \begin{cases} a_1 e^{ik_1 x} + b_1 e^{-ik_1 x}, & -\infty < x \leq x_1 \\ a_2 e^{ik_2 x} + b_2 e^{-ik_2 x}, & x_1 < x \leq x_2 \\ a_3 e^{ik_3 x} + b_3 e^{-ik_3 x}, & x_2 < x \leq x_3 \\ \dots & \dots \\ a_N e^{ik_N x} + b_N e^{-ik_N x}, & x_{N-1} < x \leq x_N \\ a_{N+1} e^{ik_{N+1} x} + b_{N+1} e^{-ik_{N+1} x}, & x_N < x < \infty \end{cases} \quad (2.42)$$

$$k_j = \sqrt{(2m/\hbar^2)(E - V_j)}.$$

We first consider the case  $E > V_1, V_{N+1}$  such that  $k_1$  and  $k_{N+1}$  are real wave vectors and  $\psi(x)$  describes running waves outside the ‘scattering region’  $[x_1, x_N]$ . Our aim now is the following: we would like to determine solutions of the Schrödinger equation, i.e. wave functions  $\psi(x)$ , under the **scattering condition**  $b_{N+1} = 0$ , i.e. we seek solutions that have only waves  $a_{N+1} e^{ik_{N+1} x}$  traveling to the right (away from the scattering zone) on the right side of the potential. On the left side, we have the wave  $a_1 e^{ik_1 x} + b_1 e^{-ik_1 x}$ , i.e. a superposition of a right-going (incoming) and a left-going (outgoing) wave. We would like to know how much of an incoming wave gets reflected on the left side (coefficient  $b_1$ ) and how much gets transmitted on the right side ( $a_{N+1}$ ).

**Step 1:** we demand that  $\psi(x)$  and its derivative  $\psi'(x)$  are continuous at  $x = x_1$ . This gives two equations

$$\begin{aligned} a_1 e^{ik_1 x_1} + b_1 e^{-ik_1 x_1} &= a_2 e^{ik_2 x_1} + b_2 e^{-ik_2 x_1} \\ a_1 e^{ik_1 x_1} - b_1 e^{-ik_1 x_1} &= (k_2/k_1)(a_2 e^{ik_2 x_1} - b_2 e^{-ik_2 x_1}) \end{aligned} \quad (2.43)$$

or

$$\begin{aligned} a_1 &= \frac{1}{2} \left( \frac{k_2}{k_1} + 1 \right) e^{i(k_2 - k_1)x_1} a_2 + \frac{1}{2} \left( 1 - \frac{k_2}{k_1} \right) e^{-i(k_2 + k_1)x_1} b_2 \\ b_1 &= \frac{1}{2} \left( 1 - \frac{k_2}{k_1} \right) e^{i(k_2 + k_1)x_1} a_2 + \frac{1}{2} \left( 1 + \frac{k_2}{k_1} \right) e^{-i(k_2 - k_1)x_1} b_2 \end{aligned} \quad (2.44)$$

which can be written in a **matrix form**

$$\mathbf{u}_1 = T^1 \mathbf{u}_2, \quad \mathbf{u}_i = \begin{pmatrix} a_i \\ b_i \end{pmatrix}, \quad i = 1, 2, \quad (2.45)$$

with

$$T^1 = \frac{1}{2k_1} \begin{pmatrix} (k_1 + k_2)e^{i(k_2 - k_1)x_1} & (k_1 - k_2)e^{-i(k_1 + k_2)x_1} \\ (k_1 - k_2)e^{i(k_2 + k_1)x_1} & (k_1 + k_2)e^{-i(k_2 - k_1)x_1} \end{pmatrix}. \quad (2.46)$$

Step 2: In completely the same manner, we obtain the **transfer matrix**  $T^2$  at the 'slice'  $x = x_2$  and

$$\mathbf{u}_2 = T^2 \mathbf{u}_3 \rightsquigarrow \mathbf{u}_1 = T^1 \mathbf{u}_2 = T^1 T^2 \mathbf{u}_3. \quad (2.47)$$

Doing this for all the slices  $x_1, \dots, x_N$ , we obtain the complete transfer matrix  $M$  that connects the wave function on the left side of the potential with the one on the right side,

$$\mathbf{u}_1 = M \mathbf{u}_{N+1}, \quad M = T^1 T^2 \dots T^N. \quad (2.48)$$

Step 3: We use the continuity equation

$$\partial_t \rho(x, t) + \partial_x j(x, t) = 0 \quad (2.49)$$

$$\rho(x, t) := \psi(x, t) \psi^*(x, t)$$

$$j(x, t) := -\frac{i\hbar}{2m} [\psi(x, t)^* \partial_x \psi(x, t) - \psi(x, t) \partial_x \psi^*(x, t)]$$

$$\psi(x, t) = \psi(x) e^{-iEt/\hbar}. \quad (2.50)$$

The current density is time-independent and can be written as

$$j(x) := -\frac{i\hbar}{2m} [\psi(x)^* \partial_x \psi(x) - \psi(x) \partial_x \psi^*(x)] = \frac{\hbar}{m} \text{Im} [\psi^*(x) \psi'(x)]. \quad (2.51)$$

The current density on the right and left side of the potential is

$$\begin{aligned} j(x > x_N) &= \frac{\hbar}{m} \text{Im}(ik_{N+1} |a_{N+1}|^2) = |a_{N+1}|^2 \frac{\hbar k_{N+1}}{m} \\ j(x < x_1) &= \frac{\hbar}{m} \text{Im} [(a_1^* e^{-ik_1 x} + b_1^* e^{ik_1 x}) i k_1 (a_1 e^{ik_1 x} - b_1 e^{-ik_1 x})] \\ &= \frac{\hbar k_1}{m} [|a_1|^2 - |b_1|^2]. \end{aligned} \quad (2.52)$$

The current density  $j(x > x_N)$  describes a particle flow to the right of the potential, 'out-flowing' to  $x \rightarrow \infty$ . On the other hand, the current density  $j(x < x_1)$  is the difference of an in-flowing positive current density and an out-flowing negative current density. The former describes an incoming particle, the latter a particle that is reflected back from the potential and returning back to  $x = -\infty$ .

Step 4: We define the **transmission coefficient**  $T$  as the ratio of the right out-flowing current density to the left in-flowing current density,

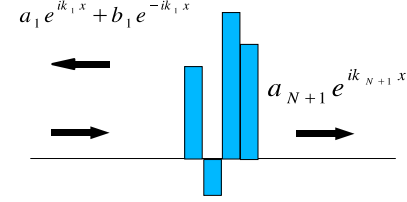
$$T := \frac{k_{N+1}}{k_1} \left| \frac{a_{N+1}}{a_1} \right|^2. \quad (2.53)$$

From

$$\begin{pmatrix} a_1 \\ b_1 \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} a_{N+1} \\ b_{N+1} \end{pmatrix} \quad (2.54)$$

and the scattering condition  $b_{N+1} = 0$  it follows

$$T = \frac{k_{N+1}}{k_1} \frac{1}{|M_{11}|^2}. \quad (2.55)$$



**Fig. 2.2:** Reflection and Transmission

To calculate the transmission coefficient through a piecewise constant one-dimensional potential, it is therefore sufficient to know the **total transfer matrix**  $M$ . The fact that  $M = T^1 T^2 \dots T^N$  is just the product of the individual two-by-two transfer matrices makes it a very convenient tool for computations.

Step 5: In completely the same manner, we define the **reflection coefficient**  $R$  as the ratio of the out-flowing current density on the left and the in-flowing (reflected) current density on the *left*, i.e.

$$R := \left| \frac{b_1}{a_1} \right|^2 = \left| \frac{M_{21}}{M_{11}} \right|^2. \quad (2.56)$$

The last equality is left as an exercise.

For eigenstates of energy  $E$  we have from the continuity equation

$$\partial_t \rho(x, t) \equiv \partial_t \rho(x) = 0 \rightsquigarrow \partial_x j(x) = 0 \rightsquigarrow j(x) = \text{const}. \quad (2.57)$$

Using Eq. (2.52) and the definition of  $T$  and  $R$ , this leads to

$$T + R = 1. \quad (2.58)$$

## 2.5 The Tunnel Effect and Scattering Resonances

In the following, we apply our theory to compute the transmission coefficient  $T$ , Eq.(2.55), to important examples of one-dimensional potentials. Before discussing the tunnel effect and scattering resonances, we consider the simpler case of a potential step.

### 2.5.1 Potential step

We consider a potential step at  $x_1 = 0$  with  $N = 1$ ,  $V_1 = 0$  and  $V_2 = V > 0$  in (2.42).

a) For  $E > V$ , we have  $k_1 = \sqrt{(2m/\hbar^2)E}$  and  $k_2 = \sqrt{(2m/\hbar^2)(E - V)}$  such that from the transfer matrix  $T_1 = M$ , Eq. (2.46), we obtain

$$M_{11} = (T_1)_{11} = \frac{1}{2} \left( 1 + \frac{k_2}{k_1} \right) e^{i(k_2 - k_1)x_1} = \frac{1}{2} \left( 1 + \frac{k_2}{k_1} \right). \quad (2.59)$$



This yields the transmission and reflection coefficients

$$\begin{aligned} T &= \frac{k_2}{k_1} \frac{1}{|M_{11}|^2} = \frac{k_2}{k_1} \frac{4k_1^2}{(k_1 + k_2)^2} = \frac{k_2}{k_1} \frac{4}{(1 + k_2/k_1)^2} = \\ &= \left[ \frac{k_2}{k_1} = \sqrt{1 - V/E} \right] = \frac{4\sqrt{1 - (V/E)}}{(1 + \sqrt{1 - (V/E)})^2} \\ R &= \left| \frac{M_{21}}{M_{11}} \right|^2 = \left| \frac{k_1 - k_2}{k_1 + k_2} \right|^2 = \frac{(1 - \sqrt{1 - (V/E)})^2}{(1 + \sqrt{1 - (V/E)})^2}, \end{aligned} \quad (2.60)$$

and we recognize that

$$T + R = 1. \quad (2.61)$$

Compare this result to the case of a classical particle running from the bottom to the top of a (soft) step: if its energy  $E$  is sufficient ( $E > V$ ), it overcomes the barrier and continues to run on the top of the step, if its energy is too small, it rolls back and is reflected. In quantum mechanics, for  $E > V$  there is a finite probability for the particle being reflected!

b) For  $E < V$  we see that  $k_2$  becomes imaginary and there are no longer running waves for  $x > 0$ : the particle then is in the classically forbidden zone. With  $k_2 = i\kappa_2$ ,  $\kappa_2 = \sqrt{(2m/\hbar^2)|E - V|}$ , the wave function on the right is  $\psi(x > 0) = a_2 e^{-\kappa_2 x} + b_2 e^{\kappa_2 x} = a_2 e^{-\kappa_2 x}$  because we had set  $b_2$  anyway. We therefore can still apply our scattering formalism to obtain the reflection coefficient

$$R = \left| \frac{k_1 - k_2}{k_1 + k_2} \right|^2 = \left| \frac{k_1 - i\kappa_2}{k_1 + i\kappa_2} \right|^2 = 1. \quad (2.62)$$

On the right side  $x > 0$ , we don't have running waves any longer for  $E < V$  and therefore cannot apply (2.55) for the transmission coefficient. The particle current density (2.51)  $j(x > 0) = 0$ , however, which means  $T = 0$ . Again, we have  $T + R = 1$ .

Compare this case to total reflection of waves in optics!

### 2.5.2 The Tunnel Barrier: Transmission Coefficient

Next, we consider a potential that has the form of a rectangular barrier. In (2.42), we set  $N = 2$ ,  $x_2 = -x_1 = a$ ,  $V_1 = V_3 = 0$ , and  $V_2 = V > 0$ . Let us recall the matrices  $T_1$  and  $T_2$  for 'step-up' and 'step-down',

$$T_1 = \frac{1}{2} \begin{pmatrix} (1+r)e^{-i\delta_- a} & (1-r)e^{i\delta_+ a} \\ (1-r)e^{-i\delta_+ a} & (1+r)e^{i\delta_- a} \end{pmatrix} \quad (2.63)$$

$$T_2 = \frac{1}{2} \begin{pmatrix} (1+1/r)e^{-i\delta_- a} & (1-1/r)e^{-i\delta_+ a} \\ (1-1/r)e^{i\delta_+ a} & (1+1/r)e^{i\delta_- a} \end{pmatrix}, \quad \delta_{\pm} \equiv k_2 \pm k_1, \quad r \equiv \frac{k_2}{k_1}. \quad (2.64)$$

We multiply the matrices  $T_1$  and  $T_2$  in order to obtain  $M = T_1 T_2$ ,

$$\begin{aligned} M &= \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \\ M_{11} &= \frac{1}{4} \left[ \frac{(1+r)^2}{r} e^{-2i\delta_- a} - \frac{(1-r)^2}{r} e^{2i\delta_+ a} \right] = \frac{1}{4} e^{2ik_1 a} \left[ \frac{(k_1^2 + k_2^2)^2}{k_1 k_2} e^{-2ik_2 a} - \frac{(k_1^2 - k_2^2)^2}{k_1 k_2} e^{2ik_2 a} \right] \\ &= e^{2ik_1 a} \left[ \frac{k_1^2 + k_2^2}{2k_1 k_2} i \sin(-2k_2 a) + \cos(2k_2 a) \right] = M_{22}^* \\ M_{12} &= \frac{k_1^2 - k_2^2}{4k_1 k_2} 2i \sin(2k_2 a) = -M_{21}. \end{aligned} \quad (2.65)$$

Use  $(k_1^2 + k_2^2)^2 = (k_1^2 - k_2^2)^2 + 4k_1^2 k_2^2$  to find

$$|M_{11}|^2 = 1 + \frac{(k_1^2 - k_2^2)^2}{4k_1^2 k_2^2} \sin^2(2k_2 a). \quad (2.66)$$

CASE 1:  $E > V$ .

In this case, both  $k_1$  and  $k_2$  are real, and we find

$$T = \frac{1}{\frac{(k_1^2 - k_2^2)^2}{4k_1^2 k_2^2} \sin^2(2k_2 a) + 1} = \frac{1}{1 + \frac{\sin^2(2\alpha\sqrt{E/V-1})}{4(E/V)(E/V-1)}}, \quad \alpha = \sqrt{\frac{2mVa^2}{\hbar^2}}. \quad (2.67)$$

CASE 2:  $E < V$ .

In this case,  $k_2 = i\kappa_2 := i\sqrt{(2m/\hbar^2)(V-E)}$  is complex, and we find

$$T = \frac{1}{\frac{(k_1^2 + \kappa_2^2)^2}{4k_1^2 \kappa_2^2} \sinh^2(2\kappa_2 a) + 1} = \frac{1}{1 + \frac{\sinh^2(2\alpha\sqrt{1-E/V})}{4(E/V)(1-E/V)}}, \quad \alpha = \sqrt{\frac{2mVa^2}{\hbar^2}}, \quad (2.68)$$

where we used

$$\sin ix = \frac{1}{2i} (e^{ix} - e^{-ix}) = i \sinh x. \quad (2.69)$$

### 2.5.3 The tunnel barrier: Discussion

For energies of the particle  $E < V$ , we have a finite transmission coefficient  $T$  that increases with  $E$ . In particular, the wave function below the barrier, i.e. in the interval  $[-a, a]$ , is non zero which means that there is a finite probability to find the particle below the barrier. This is a very important quantum mechanical phenomenon called the **tunnel effect**. Classically, a particle can not be in areas where the potential energy  $V$  is larger than its total energy  $E$ .

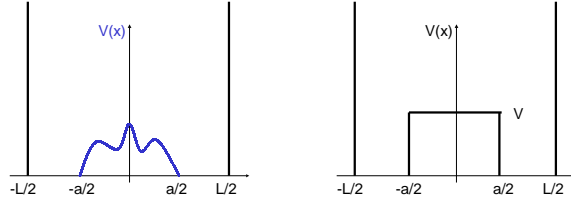
For energies of the particle  $E > V$ , the transmission coefficient oscillated as a function of energy  $E$ . At particular values of  $E$ , the  $\sin(2k_2 a)$  in (2.67) vanishes, and  $T$  exactly becomes unity. These peaks in  $T$  are called **transmission resonances**. The condition for the resonance energies is

$$\sin(2k_2 a) = 0 \rightsquigarrow 2k_2 a = n\pi \rightsquigarrow k_2 = \frac{n\pi}{2a}, \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2m(2a)^2} + V. \quad (2.70)$$

We recognize that the energies  $E_n$  are just the energy eigenvalues of the infinite potential well of width  $2a$ , shifted by the height  $V$  of the potential!

## 2.6 A more complicated case

We consider a particle of mass  $m$  confined in a one-dimensional potential well with infinitely high walls at  $x = \pm L/2$ . Within the well, i.e. within the interval  $[-a/2, a/2]$ ,  $a < L$ , there is a symmetric potential  $V(x) = V(-x) > 0$ , see Fig. 2.3. We wish to determine the stationary



**Fig. 2.3:** Left: Symmetric potential  $V(x)$  within a one-dimensional potential well. Right: special case of a rectangular potential.

bound states with energy  $E$  and the possible energy eigenvalues  $E$  for this potential. Because the potential is symmetric around the origin, the eigenstate wave functions must have even or odd parity  $\psi_{\pm}(x) = \pm\psi(-x)$ . For  $|x| > a/2$ , the wave function must be a superposition of plane waves that has to vanish at the boundaries  $\pm L/2$ . Therefore, we can set

$$\psi_{\pm}(x) = \begin{cases} A \sin k(x + L/2) = a_1 e^{ikx} + b_1 e^{-ikx} & -L/2 < x < -a/2 \\ \phi_{\pm}(x) & -a/2 < x < a/2 \\ \pm A \sin k(L/2 - x) = a_3 e^{ikx} + b_3 e^{-ikx} & a/2 < x < L/2 \end{cases}, \quad (2.71)$$

where  $A$  is a complex constant,  $k = \sqrt{(2m/\hbar^2)E}$  and  $\phi_{\pm}(x)$  the wave function within the potential region  $|x| < a/2$ . It is convenient to write the even (+) and odd (-) wave functions within one line, using the definitions

$$\begin{aligned} \psi_{\pm}(x) &= \psi_L(x) + \phi_{\pm}(x) \pm \psi_R(x), \\ \psi_L(x) &:= \begin{cases} A \sin k(x + L/2) & -L/2 < x < -a/2 \\ 0 & \text{else} \end{cases} \\ \psi_R(x) &:= \begin{cases} A \sin k(L/2 - x) & a/2 < x < L/2 \\ 0 & \text{else} \end{cases} \end{aligned} \quad (2.72)$$

Here,  $\psi_L(x)$  is localized only in the left part  $x < -a/2$  and  $\psi_R(x)$  is localized only in the right part  $x > a/2$  of the well.

We now use our transfer matrix formalism to obtain the equation that determines the possible energy values  $E$ : The solution on the left of the potential  $V(x)$  is connected to the solution on the right, cf. eq. (2.54),

$$\begin{pmatrix} a_1 \\ b_1 \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} a_3 \\ b_3 \end{pmatrix} \rightsquigarrow \begin{pmatrix} e^{ikL/2} \\ -e^{-ikL/2} \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} \mp e^{-ikL/2} \\ \pm e^{ikL/2} \end{pmatrix}.$$

Using

$$\begin{aligned} \sin k(L/2 + x) &= \frac{1}{2i} (e^{ik(L/2+x)} - e^{-ik(L/2+x)}) \\ \sin k(L/2 - x) &= \frac{1}{2i} (e^{ik(L/2-x)} - e^{-ik(L/2-x)}), \end{aligned} \quad (2.73)$$

we identify

$$\begin{aligned} a_1 &= \frac{A}{2i} e^{ikL/2}, & b_1 &= -\frac{A}{2i} e^{-ikL/2} \\ a_3 &= \mp \frac{A}{2i} e^{-ikL/2}, & b_3 &= \pm \frac{A}{2i} e^{ikL/2}, \end{aligned} \quad (2.74)$$

which yields two linear equations

$$\begin{aligned} e^{ikL/2} &= \mp M_{11} e^{-ikL/2} \pm M_{12} e^{ikL/2} \\ -e^{-ikL/2} &= \mp M_{12}^* e^{-ikL/2} \pm M_{22} e^{ikL/2}. \end{aligned} \quad (2.75)$$

Here, the upper sign always holds for the even solution  $\psi_+(x)$  while the lower sign holds for the odd solution  $\psi_-(x)$ . In fact, for a symmetric potential  $V(x) = V(-x)$ ,  $M_{22}^* = M_{11}$  and  $M_{21} = M_{12}$  such that the second of the above equations is just the conjugate complex of the first. The condition that determines the possible wave vectors  $k$  and therewith the energies  $E = \hbar^2 k^2 / 2m$  is

$$\pm 1 = -M_{11}(k) e^{-ikL} + M_{12}(k), \quad (2.76)$$

where we explicitly indicated the  $k$ -dependence of the transfer matrix elements.

### 2.6.1 Case of no potential $V(x) = 0$

In this case,

$$\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightsquigarrow \pm 1 = -e^{-ikL} \rightsquigarrow kL = \begin{cases} \pi, 3\pi, 5\pi, \dots & (+) \text{ even} \\ 2\pi, 4\pi, 6\pi, \dots & (-) \text{ odd} \end{cases} \quad (2.77)$$

**Exercise:** Check that these yield the solutions known from the infinite quantum well.

### 2.6.2 Tunnel barrier potential within well

For a rectangular tunnel barrier of width  $a$  and height  $V$ , that is  $V(x) = V\theta(a/2 - |x|)$ , we have calculated the transfer matrix  $M$  before (note that now the width is  $a$  and not  $2a$ ,  $\sin(ix) = i \sinh(x)$ , and  $\cos(ix) = \cosh(x)$ ):

$$\begin{aligned} M_{11} &= e^{ika} \left[ \cosh(\kappa a) + i \frac{\varepsilon_-}{2} \sinh(\kappa a) \right] \\ M_{12} &= i \frac{\varepsilon_+}{2} \sinh(\kappa a) \\ \varepsilon_{\pm} &:= \frac{\kappa}{k} \pm \frac{k}{\kappa}, \quad k = \sqrt{(2m/\hbar^2)E}, \quad \kappa = \sqrt{(2m/\hbar^2)(V-E)}. \end{aligned} \quad (2.78)$$

From this and Eq. (2.76), we obtain

$$\pm 1 = -e^{ik(a-L)} \left[ \cosh(\kappa a) + i \frac{\varepsilon_-}{2} \sinh(\kappa a) \right] + i \frac{\varepsilon_+}{2} \sinh(\kappa a) \quad (2.79)$$

We multiply this equation by  $e^{-ik(a-L)/2}$  and take the real part to obtain two equations for the even and the odd case. We can check that taking the imaginary part leads to the same result. Using

$$\coth(x/2) = \frac{\sinh x}{\cosh x - 1} = \frac{\cosh x + 1}{\sinh x}, \quad (2.80)$$

we obtain

$$\begin{aligned} 1 &= \frac{\kappa}{k} \tan\left(k\frac{a-L}{2}\right) \tanh\left(\frac{\kappa a}{2}\right), \quad \text{even '+'} \\ 1 &= \frac{\kappa}{k} \tan\left(k\frac{a-L}{2}\right) \coth\left(\frac{\kappa a}{2}\right), \quad \text{odd '-'}. \end{aligned} \quad (2.81)$$

Case  $V \rightarrow \infty$

In this case,  $\kappa \rightarrow \infty$  and

$$0 = \tan\left(k\frac{a-L}{2}\right) \rightsquigarrow k\frac{L-a}{2} = n\pi, \quad n = 1, 2, 3, \dots, \quad (2.82)$$

where  $(L-a)/2$  is the length of the two infinite potential wells that are completely separated by the infinitely high barrier. The wave functions in the two wells and the energies are just the ones that we have calculated for an infinite potential well.

Case  $V < \infty$  large,  $L = 2a$

We wish to see how the energies and wave functions change if we lower the central barrier from its infinite value to finite  $V$ . We already expect that due to the tunnel effect, the left and the right well, which for  $V \rightarrow \infty$  were completely separated from each other, must become coupled now. We already know the limiting cases

$$\begin{aligned} k\frac{a}{2} &= n\pi, \quad n = 1, 2, 3, \dots, \quad V \rightarrow \infty \\ k2a &= n\pi, \quad n = 1, 2, 3, \dots, \quad V = 0 \\ k &= ?, \quad 0 < V < \infty. \end{aligned} \quad (2.83)$$

Introducing dimensionless variables

$$x = ka/2, \quad \alpha := \sqrt{ma^2V/2\hbar^2}, \quad (2.84)$$

we have

$$\kappa^2 = \frac{2m}{\hbar^2}V - k^2, \quad \frac{\kappa a}{2} = \sqrt{\alpha^2 - x^2} \quad (2.85)$$

and since  $L = 2a$ ,  $\tan(k\frac{a-L}{2}) = -\tan ka/2 = -\tan x$  such that the transcendent equations (2.81) become

$$-1 = \frac{\sqrt{\alpha^2 - x^2}}{x} \tan(x) [\tanh(\sqrt{\alpha^2 - x^2})]^{\pm 1}. \quad (2.86)$$

We expand this for large  $\alpha \gg 1$  around the lowest energy solution for the case  $V \rightarrow \infty$ , that is around  $x_1 = \pi$  by setting  $x = x_1 + y$ ,  $y \ll 1$ . This yields

$$\begin{aligned} -1 &\approx \frac{\alpha}{x_1 + y} \tan(x_1 + y) [\tanh \alpha]^{\pm 1} \approx \frac{\alpha}{\pi} y [\tanh \alpha]^{\pm 1} \\ &\rightsquigarrow y \approx -\frac{\pi}{\alpha} [\tanh \alpha]^{\mp 1} \rightsquigarrow x \approx \pi \left(1 - \frac{1}{\alpha} [\tanh(\alpha)]^{\mp 1}\right). \end{aligned} \quad (2.87)$$

The corresponding wave vectors for the lowest energy solution therefore are

$$k_+ \approx \frac{2\pi}{a} \left(1 - \frac{1}{\alpha \tanh(\alpha)}\right), \quad k_- \approx \frac{2\pi}{a} \left(1 - \frac{\tanh(\alpha)}{\alpha}\right). \quad (2.88)$$

Since  $\tanh \alpha < 1$ , we recognize  $k_+ < k_-$ . Compared with the case  $V \rightarrow \infty$  where the lowest  $k$  was  $k = 2\pi/a$ , we now have a **splitting** into two different  $k$ 's. The lowest symmetric (even) wave function has an energy  $E_+ = \hbar^2 k_+^2/2m$  that is lower than the energy  $E_- = \hbar^2 k_-^2/2m$  of the lowest odd wave function. This **level splitting** is an important general feature appearing when two regions in space become coupled by the tunnel effect.

For very large  $V$ , the wave functions that belong to  $k_{\pm}$  below the barrier must be very small: we see that as  $\alpha \rightarrow \infty$ ,  $\Psi_{\pm}(x = \pm a/2) \rightarrow 0$  whence by continuity also the central part of the wave function  $\phi_{\pm}(x)$  must become very small. Then, we can approximate the wave functions for the two lowest energies  $E_{\pm}$  as

$$\psi_{\pm}(x) = \psi_L(x) \pm \psi_R(x), \quad (2.89)$$

where in the definition of the left and right part wave functions  $\psi_{L/R}(x)$  we have to use  $k_+$  for the even and  $k_-$  for the odd solution. In fact, for large  $V$ , Eq. (2.88) tells us that the  $k_{\pm}$  are very close to the wave vector  $k = 2\pi/a$  of the infinite-barrier limit, cf. Eq. (2.83), and therefore the  $\psi_{L/R}(x)$  are very close to the lowest sin-wave functions of the left and right well.

## 3. THE STRUCTURE OF QUANTUM MECHANICS

### 3.1 Axioms of Quantum Mechanics and the Hilbert Space

In this and the following sections, we summarize the main assumptions underlying quantum mechanics and clarify its mathematical structure. We will discuss the concept of the **Hilbert space** of quantum states, orthogonality and superposition of wave functions, and the representation of physical variables like the momentum or the energy as operators. This slightly more abstract point of view will help us enormously to extend the theory to many other physical systems, and to find a clear language for describing them.

In the preceding section we have already introduced all the required components we need to construct the main theory.

#### 3.1.1 Recalling our axioms

In *classical mechanics*, as described by Newton's equations, a central mathematical object is the **phase space**, that is the space of all coordinates and momenta  $(x_i, p_i)$  of the particles to be described.

Example: A harmonic oscillator of mass  $m$  and angular frequency  $\omega$  has the energy  $H = E = p^2/2m + (1/2)m^2\omega^2x^2$ . For constant energy  $E$ , its phase space is therefore an ellipse in the  $p - x$ -plane.

On the other hand, according to Planck, the possible energies of an oscillator are quantized,  $E = n\hbar\omega$ . In the early days of quantum mechanics, people tried to go on with the concept of the phase space, particle trajectories, and to combine it with quantization rules. However, it became obvious very soon that a more powerful and fundamental theory was needed to explain the spectral lines of atoms. Werner Heisenberg was the one who finally made the breakthrough in 1925 when he stayed a few weeks on the small island of Helgoland in order to cure an attack of hay fever. At that time, he tried to solve a slightly more difficult, non-linear version of the *harmonic oscillator*. He came up with the idea that instead of trying to find all the trajectories of, for example, electrons in an atom, one should rather consider the entirety of all the frequencies of the spectral lines and their intensities to replace the concept of 'trajectories'. This in any case should be more natural since it is the frequencies and intensities which can be observed, not the trajectories of the electrons.

This meant in particular that the concept of the phase space no longer holds in a quantum theory. We already know what one has instead: it is the entity of wave functions that are solutions of the Schrödinger equation. Its stationary solutions at certain energy eigenvalues form the basis of this linear space of wave functions, the Hilbert space  $\mathcal{H}$ . We had already discussed an example of a Hilbert space for the solutions of the infinitely high potential well.

If you get lost in the following, always have this example in mind:

Example: The solutions of the stationary Schrödinger equation for the infinite potential well

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad E = E_n = \frac{n^2\hbar^2\pi^2}{2mL^2}, \quad n = 1, 2, 3, \dots$$

We have learned how to work with wave functions, to calculate probabilities, transmission and reflection coefficients, possible energy values etc. In the following two or three more abstract sections, the wave functions are regarded as vectors, i.e. elements of a vector space.

You certainly know what a vector space is; always have in mind the three-dimensional real vector space  $R^3$  where one can add and subtract vectors  $\mathbf{x}$ , and multiply vectors with real numbers. The vector spaces of quantum mechanics in general are complex (i.e. you multiply vectors with complex numbers) and, in contrast to  $R^3$ , often of infinite dimension. But this is not very astonishing to us as we already know by heart our example wave functions  $\psi_n$  of the potential well, which form an infinitely dimensional basis.

For convenience, we recall the table we used earlier:

Example	vectors and matrices	Particle in Quantum Well
vector	$\mathbf{x}$	wave function $\psi(x)$
space	vector space	Hilbert space
linear operator	matrix $A = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	Hamiltonian $H_{\text{well}}$
eigenvalue problem	$A\mathbf{x} = \lambda\mathbf{x}$	$H_{\text{well}}\psi_n = E_n\psi_n$
eigenvalue	$\lambda_1 = 1, \lambda_2 = -1$	$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}, n = 1, 2, 3, \dots$
eigenvector	$\mathbf{x}_{1,2} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$	wave function $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$
scalar product	$\langle \mathbf{x}   \mathbf{y} \rangle \equiv \sum_{n=1}^2 x_n^* y_n$	$\langle \psi   \phi \rangle \equiv \int_0^L dx \psi^*(x) \phi(x)$
orthogonal basis	$\langle \mathbf{e}_n   \mathbf{e}_m \rangle = \delta_{nm}$	$\langle \psi_n   \psi_m \rangle = \delta_{nm}$
dimension	2	$\infty$
completeness	$\mathbf{x} = \sum_{n=1}^2 \langle \mathbf{e}_n   \mathbf{x} \rangle \mathbf{e}_n$	$\psi = \sum_{n=1}^{\infty} \langle \psi_n   \psi \rangle \psi_n$
vector components	$\mathbf{x} = (\langle \mathbf{e}_1   \mathbf{x} \rangle, \langle \mathbf{e}_2   \mathbf{x} \rangle)$	$\psi = (\langle \psi_1   \psi \rangle, \langle \psi_2   \psi \rangle, \dots)$

#### 3.1.2 Math: The Hilbert Space

We start with a few mathematical terms that are necessary for the definition of a Hilbert space.

Def.: A norm  $\|\cdot\|$  is a mapping of a complex vector space  $V$  into the real numbers  $R_+$ , such that for elements  $\psi, \phi \in V$

$$\begin{aligned} \|\psi\| &\geq 0, & \|\psi\| = 0 &\leftrightarrow \psi = 0 \\ \|c\psi\| &= |c| \|\psi\|, & c &\in \mathbb{C} \\ \|\psi + \phi\| &\leq \|\psi\| + \|\phi\| \end{aligned} \quad (3.1)$$

Def.: A scalar product is a mapping of a pair of vectors  $\psi, \phi$  to a complex number  $\langle \psi | \phi \rangle$  such that for arbitrary  $\psi, \phi, \chi \in V$

$$\begin{aligned} \langle \psi | \psi \rangle &\geq 0 \\ \langle \psi | c\phi \rangle &= c\langle \psi | \phi \rangle, \quad c \in \mathbb{C} \\ \langle \psi + \phi | \chi \rangle &= \langle \psi | \chi \rangle + \langle \phi | \chi \rangle \\ \langle \psi | \phi \rangle &= \langle \phi | \psi \rangle^* \end{aligned} \quad (3.2)$$

Def.: A vector space with scalar product and norm  $\|\psi\| = \sqrt{\langle \psi | \psi \rangle}$  is called **unitary space**.

Def.: A sequence  $\{\psi_n\}$  in a unitary space is called **Cauchy sequence**, if with all real number  $\varepsilon > 0$  there is an integer  $N(\varepsilon)$  such that for all  $n, m > N(\varepsilon)$ ,  $\langle \psi_n | \psi_m \rangle < \varepsilon$  holds.

Def.: A unitary space  $X$  is called **complete**, if each Cauchy sequence in  $X$  converges to a vector  $\psi \in X$ .

Def.: A **Hilbert space** is a complete unitary space.

### 3.1.3 Math: Examples of Hilbert spaces

The  $d$ -dimensional Hilbert space  $\mathcal{H} = R^d$

This vector space has a basis of unit vectors  $\mathbf{e}_n$ ,

$$\mathbf{e}_1 = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad \dots, \quad \mathbf{e}_d = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 1 \end{pmatrix}. \quad (3.3)$$

Vectors are columns and in printed text written as the transposed (symbolized by  $T$  that is sometimes omitted) of lines  $\mathbf{x} = (x_1, \dots, x_d)^T$ . The scalar product of two vectors  $\mathbf{x} = (x_1, \dots, x_d)^T, \mathbf{y} = (y_1, \dots, y_d)^T$ , is  $\langle \mathbf{x} | \mathbf{y} \rangle = \sum_{n=1}^d x_n y_n$ . Each vector  $\mathbf{x} = (x_1, \dots, x_d)^T \in R^d$  can be decomposed into

$$\mathbf{x} = \sum_{n=1}^d \langle \mathbf{e}_n | \mathbf{x} \rangle \mathbf{e}_n. \quad (3.4)$$

The Hilbert space  $\mathcal{H} = \mathcal{H}_{\text{well}}$

This is the space of square integrable wave functions  $\psi(x)$  of the infinite potential well, section 2.2, defined on the interval  $[0, L]$ , with  $\psi(x) = \psi(L) = 0$ . Each function  $\psi$  is considered as a vector, the linear structure of a vector space comes from the fact the  $\psi \in \mathcal{H}, \phi \in \mathcal{H} \Rightarrow \psi + \phi, c\psi \in \mathcal{H}$ . **The scalar product is given by an integral**

$$\langle \psi | \phi \rangle := \int_0^L dx \psi^*(x) \phi(x). \quad (3.5)$$

You can check that this is a scalar product indeed. The eigenvectors of the Hamiltonian  $\hat{H}$ , i.e. the functions  $\phi_n(x)$  with energy  $E_n$ ,

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad E_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2}, \quad n = 1, 2, 3, \dots \quad (3.6)$$

form an orthonormal basis of  $\mathcal{H}$

$$\langle \psi_n | \psi_m \rangle = \delta_{nm}. \quad (3.7)$$

Any wave function  $f \in \mathcal{H}$  can be expanded into a linear combination of basis vectors, i.e. eigenfunctions  $\psi_n$ ,

$$f = \sum_{n=1}^{\infty} \langle \psi_n | f \rangle \psi_n. \quad (3.8)$$

We summarize the above two examples in the following table:

example	$R^d$	$\mathcal{H}_{\text{well}}$
vector	$\mathbf{x}$	wave function $\psi$
scalar product	$\langle \mathbf{x}   \mathbf{y} \rangle = \sum_{n=1}^d x_n^* y_n$	$\langle \psi   \phi \rangle := \int_0^L dx \psi^*(x) \phi(x)$
orthonormal basis	$\langle \mathbf{e}_n   \mathbf{e}_m \rangle = \delta_{nm}$	$\langle \psi_n   \psi_m \rangle = \delta_{nm}$
completeness	$\mathbf{x} = \sum_{n=1}^d \langle \mathbf{e}_n   \mathbf{x} \rangle \mathbf{e}_n$	$\psi = \sum_{n=1}^{\infty} \langle \psi_n   \psi \rangle \psi_n$
components	$\mathbf{x} = (\langle \mathbf{e}_1   \mathbf{x} \rangle, \dots, \langle \mathbf{e}_d   \mathbf{x} \rangle)$	$\psi = (\langle \psi_1   \psi \rangle, \langle \psi_2   \psi \rangle, \dots)$

If you understand this table, you are already halfway in completely understanding the math underlying quantum mechanics.

### 3.1.4 First Axiom: States as Hilbert Space Vectors

To conclude, we formulate our first axiom of quantum mechanics:

**Axiom 1:** A quantum mechanical system is described by a vector  $|\Psi(t)\rangle \equiv \Psi(t)$  of a Hilbert space  $\mathcal{H}$ . The time evolution of  $\Psi(t)$  is determined by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = \hat{H} \Psi(t) \quad (3.9)$$

The Hamilton operator  $\hat{H}$  is an operator corresponding to the total energy of the system. In the case of a single particle with mass  $m$  moving in the configuration space  $R^d$  under a potential  $V(\mathbf{x})$ , the wave function  $\Psi(\mathbf{x}, t) \in \mathcal{H} = L^2(R^d)$  (square integrable functions) obeys

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{x}, t) = \left[ -\frac{\hbar^2 \Delta}{2m} + V(\mathbf{x}) \right] \Psi(\mathbf{x}, t). \quad (3.10)$$

$|\Psi(\mathbf{x}, t)|^2 d^d x$  is the probability for the particle to be in the (infinitesimal small) volume  $d^d x$  around  $\mathbf{x}$  at time  $t$ . The solutions of the stationary Schrödinger equation at fixed energy,

$$\hat{H} \phi = E \phi \quad (3.11)$$

are called **stationary states**, the possible energies  $E$  eigenenergies.

Note that the form of the Hamilton operator not necessarily has to be as in (3.10), the Hamiltonian for a single particle defined over the space  $R^d$ . We will later encounter, for example, Hamiltonians that describe the sites of a finite lattice and have the form of a  $n \times n$  matrix.

### 3.1.5 Math: Completeness, Dirac notation

*Def.:* An orthonormal basis  $\{\psi_n\}$ ,  $\langle\psi_n|\psi_m\rangle = \delta_{nm}$ , of a Hilbert space is called **complete** if no vector  $\phi$  (except the zero vector) is orthogonal to all  $\psi_n$ .

In the following, we will mostly deal with Hilbert spaces that have a complete orthonormal basis, which guarantees the expansion of any wave function into a linear combination of basis vectors. In most cases, the orthonormal basis consists of the eigenfunctions (eigenvectors) of the Hamilton operator  $\hat{H}$ .

In quantum mechanics it has become common to use the symbol ('ket')  $|\psi\rangle$  for a wave function (Hilbert space vector) instead of  $\psi$ . The expansion of an arbitrary ket  $|\psi\rangle$  into the orthonormal basis  $\{|\psi_n\rangle; n = 0, 1, 2, 3, \dots\}$  then can be written as

$$|\psi\rangle = \sum_{n=0}^{\infty} |\psi_n\rangle \langle\psi_n|\psi\rangle. \quad (3.12)$$

Here, the scalar product, that is the 'bracket'  $\langle\psi_n|\psi\rangle$ , gives rise to define the bra vector (from 'bra-cket')  $\langle\psi_n|$  as the state with wave function  $\psi_n^*(x)$ . This means that

$$\langle\psi| = \sum_{n=0}^{\infty} \langle\psi_n|\langle\psi|\psi_n\rangle. \quad (3.13)$$

A very convenient way to memorize and use the completeness property is the '**insertion of the 1**',

$$1 = \sum_{n=0}^{\infty} |\psi_n\rangle \langle\psi_n| \rightsquigarrow |\psi\rangle = 1|\psi\rangle = \sum_{n=0}^{\infty} |\psi_n\rangle \langle\psi_n|\psi\rangle. \quad (3.14)$$

## 3.2 Operators and The Two-Level-System I

### 3.2.1 Operators

Quantum mechanics is a theory of probabilities and expectation values for the outcomes of experiments. We have already learned how to use the wave function to calculate expectation values of the position  $\mathbf{x}$ , the momentum  $\mathbf{p}$ , or any function of these, cf. Eq. (1.64).

We now slightly generalize our axiom 2:

**Axiom 2a:** In quantum mechanics, physical quantities like position, momentum, angular momentum, kinetic energy, total energy etc. correspond to **linear operators**  $A$  that act on Hilbert space vectors. The position  $\mathbf{x}$  corresponds to the operator 'multiplication with  $\hat{\mathbf{x}}$ ', the momentum  $\mathbf{p}$  to the operator  $-i\hbar\nabla$ . Any other quantity depending on  $\mathbf{x}$  and  $\mathbf{p}$  becomes an operator  $\hat{O}(\hat{\mathbf{x}}, \hat{\mathbf{p}})$  by this **correspondence principle**  $\mathbf{x} \rightarrow \hat{\mathbf{x}}$  and  $\mathbf{p} \rightarrow -i\hbar\nabla$ . The commutation relation

$$\begin{aligned} [\hat{x}_k, \hat{p}_l] &= i\hbar\delta_{kl} \\ \delta_{kl} &:= 1, \quad k = l, \quad \text{and } 0 \text{ else} \end{aligned} \quad (3.15)$$

holds.

Expectation values at time  $t$  of any operator  $A$  for a quantum mechanical system described by a vector  $|\psi(t)\rangle$  in a Hilbert space (for example, a wave function  $\Psi(\mathbf{x}, t)$ ), are defined by

applying  $A$  on  $|\Psi(t)\rangle$  and calculating the Hilbert space scalar product

$$\langle A \rangle_t := \frac{\langle\Psi(t)|A|\Psi(t)\rangle_t}{\langle\Psi(t)|\Psi(t)\rangle_t}. \quad (3.16)$$

### 3.2.2 Examples for Expectation Values

For a quantum mechanical system described by a normalized wave function  $\Psi(\mathbf{x}, t)$ , the expectation value of an operator  $\hat{O}(\hat{\mathbf{x}}, \hat{\mathbf{p}})$  is

$$\langle O(\hat{\mathbf{x}}, \hat{\mathbf{p}}) \rangle_t = \int d^d x \Psi^*(\mathbf{x}, t) O(\hat{\mathbf{x}}, \hat{\mathbf{p}}) \Psi(\mathbf{x}, t). \quad (3.17)$$

Here,  $d$  denotes the dimension of the configuration space. For example, in  $d = 1$  dimension we have

$$\begin{aligned} \langle x \rangle_t &= \int dx \Psi^*(x, t) x \Psi(x, t), \quad \text{position} \\ \langle p \rangle_t &= \int dx \Psi^*(x, t) \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi(x, t), \quad \text{position} \end{aligned} \quad (3.18)$$

### 3.2.3 Matrix Operators and The Two-Level System

We have already seen how confinement of particles leads to discrete energies  $E_n$  and wave functions localized to certain regions of space. Furthermore, we have learned that the coupling of two separated quantum systems (like the potential wells in section 2.6) leads to the splitting of energy levels. The tunnel effect couples the left and the right well and leads to new states that are superpositions, cf. (2.89),

$$\psi_{\pm}(x) = \psi_L(x) \pm \psi_R(x). \quad (3.19)$$

We had seen furthermore that the derivation of this result, starting from the one-dimensional Schrödinger equation, is quite lengthy, because transcendental equations for the possible energies have to be solved at least approximatively. We therefore would like to find a simpler, slightly more abstract model, that describes the main physics of the level splitting and the tunnel effect, leading to eigenstates like the  $\psi_{\pm}$  above.

We consider again a system where a particle is moving in a potential that has the form of a **double well** like the one in section 2.6. We are interested in the case where the barrier between the two wells is very high. Let us concentrate on the wave functions with the lowest energies. We know already that we can express them approximately by the linear combinations  $\psi_{\pm}$  of the two lowest states  $\psi_L(x)$  and  $\psi_R(x)$  of the left and the right well.

We now perform the 5 steps that establish a simple model of what is going on when the two wells become coupled by the barrier:

**STEP 1:** starting from two isolated wells, we completely neglect all states apart from the two ground states in the two wells,  $\psi_L(x)$  and  $\psi_R(x)$ . We are only interested in the 'low-energy' sector. If both wells have a small width, we know that the next eigenvalue of the energy is far above the ground state energy so that all other states are energetically far away from the two ground states  $\psi_L(x)$  and  $\psi_R(x)$ .

**STEP 2:** we now define these two ground states as the two basis vectors of a complex two-dimensional Hilbert space  $\mathcal{H} = \mathcal{C}^2$ . We try to discuss all the following quantum mechanical

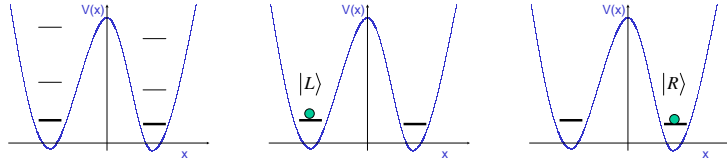


Fig. 3.1: Double well potential (left) and its two lowest states.

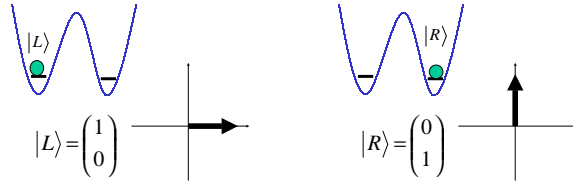


Fig. 3.2: Vector representation of left and right lowest states of double well potential.

features within this ‘small’ Hilbert space which shall be our approximation of what ‘really is going on’.

STEP 3: we call the basis vectors  $|L\rangle$  (corresponding to the wave function  $\psi_L(x)$ ) and  $|R\rangle$  (corresponding to the wave function  $\psi_R(x)$ ). We consider  $|R\rangle$  and  $|L\rangle$  just as basis vectors of  $C^2$ . The particular form of the corresponding wave functions does not interest us. We rather introduce the notation for basis vectors known from linear algebra, that is

$$|L\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |R\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (3.20)$$

The scalar product in  $\mathcal{H} = C^2$  is the standard scalar product for vectors: although the basis vectors  $|L\rangle$  and  $|R\rangle$  correspond to the two wave functions in the left and right well, here they are really vectors. In our abstract model we don’t care a hell about what  $|L\rangle$  and  $|R\rangle$  stand for.

STEP 4: We associate a Hamiltonian  $\hat{H}_0$  with the two isolated wells: trivially, the particle is either in the left or in the right well. A measurement of the energy (the observable belonging to  $\hat{H}_0$ ) yields one of the eigenvalues of  $\hat{H}_0$ , i.e.  $E_L$  (the energy of the lowest state left) or  $E_R$  (the energy of the lowest state right). In fact, in section 2.6 we always had  $E_L = E_R$  but let us be a bit more general here and allow different ground state energies in both isolated wells. The Hamiltonian is a two-by-two matrix,

$$\hat{H}_0 = \begin{pmatrix} E_L & 0 \\ 0 & E_R \end{pmatrix} \quad (3.21)$$

because with this form

$$\hat{H}_0|L\rangle = E_L|L\rangle, \quad \hat{H}_0|R\rangle = E_R|R\rangle, \quad (3.22)$$

that is  $|L\rangle$  is eigenvector with eigenvalue  $E_L$  and  $|R\rangle$  is eigenvector with eigenvalue  $E_R$ .

STEP 5 (this is the most abstract step): we now want to incorporate the tunnel effect when the two wells become coupled by a barrier of finite height. What is the total Hamiltonian  $\hat{H}$  of the system then? A particle initially localized in the left well can now tunnel into the right well and vice versa. The time-evolution of the wave function is determined by the total Hamiltonian (remember the time-dependent Schrödinger equation!) which therefore must contain a term like

$$\hat{T} := \begin{pmatrix} 0 & T \\ T^* & 0 \end{pmatrix} \rightsquigarrow \hat{T}|L\rangle = T^*|R\rangle, \quad \hat{T}|R\rangle = T|L\rangle. \quad (3.23)$$

The operator  $\hat{T}$  changes  $|L\rangle$  into  $|R\rangle$  and  $|R\rangle$  into  $|L\rangle$ , i.e. it puts the particle from the left to the right and from the right to the left which mimics the tunnel process. The strength of this process is proportional to  $T$  which is a free complex parameter in this model.

Furthermore, the energies  $E_L$  and  $E_R$  are changed: we therefore write the total Hamiltonian as a sum of three terms,

$$\hat{H} = \begin{pmatrix} E_L & 0 \\ 0 & E_R \end{pmatrix} + \begin{pmatrix} \delta\varepsilon_L & 0 \\ 0 & \delta\varepsilon_R \end{pmatrix} + \begin{pmatrix} 0 & T \\ T^* & 0 \end{pmatrix} =: \begin{pmatrix} \varepsilon_L & T \\ T^* & \varepsilon_R \end{pmatrix}. \quad (3.24)$$

We check first that  $\hat{H}$  is hermitian as it must be: this is the reason why we have  $T^*$  as  $\hat{H}_{21}$ .

The two-by-two matrix Hamiltonian  $\hat{H}$ , (3.24), is called the Hamiltonian of the two-level system. It describes the simplest possible quantum mechanical system in terms of the three parameters  $\varepsilon_L$ ,  $\varepsilon_R$ , and  $T$ . In spite of its simplicity, this model is the basis for a lot of phenomena in different fields of physics, such as the dynamics of emission and absorption of light from atoms, the nuclear magnetic resonance (NMR), the spin 1/2 of particles, the physics of semiconductors with two bands (valence and conduction band), and many others.

### 3.3 Operators and Measurements

We start with some general definitions.

#### 3.3.1 Math: Linear Operators

*Def.:* A linear Operator  $A$  acting on vectors  $|\psi\rangle, |\phi\rangle$  of a Hilbert space  $\mathcal{H}$  has the property

$$A[|\psi\rangle + c|\phi\rangle] = A|\psi\rangle + cA|\phi\rangle, \quad c \in C. \quad (3.25)$$

Examples for linear operators: 1.  $(n \times n)$ -matrices  $A$ , acting on vectors  $\mathbf{x} \rightarrow A(\mathbf{x})$  (linear mappings)

2. The momentum operator  $\hat{\mathbf{p}}$ , acting on a Hilbert space of differentiable functions as

$$\hat{\mathbf{p}} : f \rightarrow \hat{\mathbf{p}}f, \quad \hat{\mathbf{p}}f(\mathbf{x}) = \frac{\hbar}{i}\nabla f(\mathbf{x})$$

Example for a nonlinear operator: the operator that squares a function  $f$ ,  $A : f \rightarrow f^2$ .

Expectation values of observables  $A$  in particular should be real numbers because they represent the outcome of an average over many measurements. We have to introduce one additional definition to clarify this concept:

*Def.:* The adjoint operator  $A^\dagger$  of a linear operator  $A$  acting on a Hilbert space  $\mathcal{H}$  is defined by

$$\langle \psi | A \phi \rangle = \langle A^\dagger \psi | \phi \rangle, \quad \forall \phi, \psi \in \mathcal{H}. \quad (3.26)$$

*Def.:* A linear operator  $A$  on the Hilbert space  $\mathcal{H}$  is called **hermitian**, if the following relation holds:

$$\langle A \psi | \phi \rangle = \langle \psi | A \phi \rangle, \quad \forall \phi, \psi \in \mathcal{H}. \quad (3.27)$$

Examples:

1. For complex two-by-two matrices

$$A = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \rightsquigarrow A^\dagger = \begin{pmatrix} a^* & c^* \\ b^* & d^* \end{pmatrix}.$$

This means that the adjoint matrix  $A^\dagger$  of a given matrix  $A$  is given by the transposed conjugate complex of  $A$ , i.e.  $A^\dagger = (A^*)^T$ .

2. For complex two-by-two matrices

$$A = \begin{pmatrix} a & b \\ c & d \end{pmatrix} = A^\dagger \rightsquigarrow a = a^*, d = d^*, b^* = c.$$

3. The momentum operator  $\hat{p}$  in one dimension, acting on wave functions  $\psi(x), \phi(x), x \in \mathbb{R}$  that vanish at  $x \rightarrow \pm\infty$ , is hermitian:

$$\langle \psi | \hat{p} \phi \rangle = -i\hbar \int dx \psi^*(x) [\phi(x)]' = \int dx [-i\hbar \psi'(x)]^* \phi(x) = \langle \hat{p} \psi | \phi \rangle.$$

The expectation values of hermitian operators  $A$  in any Hilbert space state vector  $\psi$  are real indeed because

$$\langle A \rangle = \langle \psi | A \psi \rangle = \langle A \psi | \psi \rangle = \langle \psi | A \psi \rangle^* = \langle A \rangle^*. \quad (3.28)$$

This gives rise to the second part of axiom 2:

**Axiom 2b:** Physical observable quantities correspond to **hermitian linear operators**  $A$  acting on Hilbert space vectors.

Furthermore, the following theorem holds:

*Theorem:* The eigenvalues of hermitian operators  $A$  are real. This is because

$$A|\psi\rangle = \lambda|\psi\rangle \rightsquigarrow \lambda = \frac{\langle \psi | A | \psi \rangle}{\langle \psi | \psi \rangle} \in \mathbb{R}. \quad (3.29)$$

This leads us to the most central part of our axioms:

### 3.3.2 Eigenvalues and Measurement

We now arrive at one of the most important concepts of quantum mechanics: the possible outcomes of a measurement of a quantity corresponding to  $A$  are only the eigenvalues of  $A$ . After the measurement the system is in an eigenstate of  $A$  with a predictable probability depending on  $A$  and its state just before the measurement.

These two statements belong to the **Kopenhagen interpretation** of quantum mechanics and are widely accepted and experimentally confirmed by now. They belong to the axioms of quantum mechanics and can be motivated as follows:

Consider a quantum mechanical system in a normalized state  $|\psi\rangle$ . We wish to perform a measurement of a quantity (for example the energy) that is represented by a hermitian operator  $A$  (for example the Hamiltonian  $\hat{H}$ ).

CASE 1: Assume that  $|\psi\rangle = |\phi\rangle$  is an eigenstate of  $A$ ,  $A|\phi\rangle = \lambda|\phi\rangle$  with eigenvalue  $\lambda$ . Repeating this measurement at many systems that are prepared in the same way, or at the same system that is always prepared in the same state  $|\phi\rangle$ , the expectation value of  $A$  is  $\langle A \rangle = \lambda$ .

CASE 2: Assume that  $|\psi\rangle$  is not an eigenstate of  $A$ . After a measurement with outcome  $a$  assume the system is in another state  $|\phi\rangle$ . Assume immediately after the first measurement, a second measurement with outcome  $b$  is performed. We now *assume* that this second measurement should give the same outcome as the first measurement, i.e.  $a = b$ . This thought experiment is repeated many times at identically prepared systems. Always  $b = a$  should come out such that the square deviation of  $A$  for the state  $|\phi\rangle$  is zero:

$$\langle [A - \langle A \rangle]^2 \rangle = \frac{\langle \phi | [A - a]^2 | \phi \rangle}{\langle \phi | \phi \rangle} = 0 \rightsquigarrow (A - a)|\phi\rangle = 0.$$

This tells us that after the first measurement, the system is in an eigenstate  $|\phi\rangle$  of  $A$ , and the outcome of this measurement is an eigenvalue  $a$  of  $A$ . The second measurement then is as in case 1 and yields  $a$  with the system remaining in the eigenstate  $|\phi\rangle$ .

**Axiom 2c:** The possible outcomes of measurements of an observable corresponding to the hermitian linear operators  $A$  are the eigenvalues of  $A$ . Immediately after the measurement, the quantum system is in the eigenstate of  $A$  corresponding to the eigenvalue that is measured.

This axiom is the most radical break with classical physics: it postulates an abrupt collapse of the wave function (“**reduction of the wave packet**”) into one of the eigenstates of  $A$ , if a measurement is performed. Before the measurement is actually done, one can not predict its outcome, that is which eigenvalue is measured. Only probabilities for the possible outcomes can be predicted:

**Axiom 2d:** Let  $A$  have a complete system of eigenvectors  $\{|\phi_n\rangle\}$  with eigenvalues  $a_n$ . The normalized state  $|\psi\rangle$  before the measurement of  $A$  can be expanded into

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n |\phi_n\rangle, \quad c_n = \langle \phi_n | \psi \rangle \in \mathbb{C}. \quad (3.30)$$

Then, the expectation value of  $A$  in  $|\psi\rangle$  is

$$\langle \psi | A | \psi \rangle = \sum_{n=0}^{\infty} a_n |c_n|^2 =: \sum_{n=0}^{\infty} a_n p_n, \quad (3.31)$$

and the probability  $p_n$  to find the system in the eigenstate  $|\phi_n\rangle$  after the measurement is given by the amplitude square  $p_n = |c_n|^2 = |\langle \phi_n | \psi \rangle|^2$ .



### 3.3.3 Example: Position Measurement in the Two-Level system

We have seen above that a particle in the a double well potential can be described by a vector  $|\psi\rangle$  in the Hilbert space  $\mathcal{H} = C^2$ ,

$$|\psi\rangle = c_0|L\rangle + c_1|R\rangle = c_0 \begin{pmatrix} 1 \\ 0 \end{pmatrix} + c_1 \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad c_0, c_1 \in C, |c_0|^2 + |c_1|^2 = 1. \quad (3.32)$$

The last condition  $|c_0|^2 + |c_1|^2 = 1$  means that the state  $|\psi\rangle$  is normalized. What is the meaning of the coefficients  $c_0$  and  $c_1$ ?

CASE 1:  $c_0 = 1, c_1 = 0$ : The particle is in the state  $|\psi\rangle = |L\rangle$ , which means it is in the left well.

CASE 2:  $c_0 = 0, c_1 = 1$ : The particle is in the state  $|\psi\rangle = |R\rangle$ , which means it is in the right well.

We define the operator (two-by-two matrix)

$$A := \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (3.33)$$

Its eigenvectors are the two basis vector  $|L\rangle$  and  $|R\rangle$ :

$$\begin{aligned} A|L\rangle &\equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 1 \cdot \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ A|R\rangle &\equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = -1 \cdot \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \end{aligned} \quad (3.34)$$

The operator  $A$  thus corresponds to the measurement ‘where is the particle, in the left or in the right well’. This is the simplest version of a position measurement, where we are not interested in the precise position, but only measure in which well the particle is. For example, if the particle is charged with the elementary charge  $-e$ , we could measure the charge in the left well. If the particle is in there, we find  $-e$ , if it is in the right well, we find 0.

We now apply our axiom 2d to this ‘position measurement’: we cite it here in the form that exactly matches our two-level system:

**Axiom 2d:** Let  $A$  have a complete system of eigenvectors  $\{|\phi_0\rangle = |L\rangle, |\phi_1\rangle = |R\rangle\}$  with eigenvalues  $a_0 = 1, a_1 = -1$ . The normalized state  $|\psi\rangle$  before the measurement of  $A$  can be expanded into

$$|\psi\rangle = \sum_{n=0}^1 c_n |\phi_n\rangle = c_0|L\rangle + c_1|R\rangle. \quad (3.35)$$

Then, the expectation value of  $A$  in  $|\psi\rangle$  is

$$\langle\psi|A|\psi\rangle = \sum_{n=0}^1 a_n |c_n|^2 = \sum_{n=0}^1 a_n p_n, \quad (3.36)$$

and the probability  $p_n$  to find the system in the eigenstate  $|\phi_n\rangle$  after the measurement is given by the amplitude square  $p_n = |c_n|^2$ .

We therefore recognize:

$$\begin{aligned} |c_0|^2 = p_0 &= \text{the probability to find the particle in the left well} \\ |c_1|^2 = p_1 &= \text{the probability to find the particle in the right well.} \end{aligned} \quad (3.37)$$

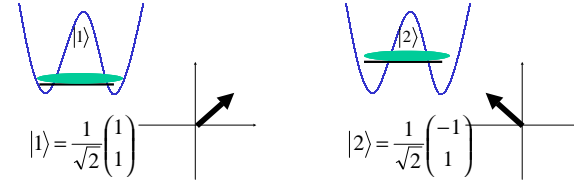


Fig. 3.3: New hybridized basis states of the double well potential.

In particular, the probability to find the particle in either the left or the right well is  $p_0 + p_1 = |c_0|^2 + |c_1|^2 = 1$  as it must be. For example, if we perform the measurement by measuring an extra charge in the left well, we find  $-e$  with probability  $|c_0|^2$ , and after the measurement the particle is in the left well, that is in the state  $|L\rangle$ . If, on the other hand, we find an extra charge 0 in the left well, the particle must be in the right well, that is in the state  $|R\rangle$ . The probability for this is  $1 - |c_0|^2 = |c_1|^2$ .

## 3.4 Energy Measurements

### 3.4.1 Eigenstates of the Two-Level System

In the previous section we had seen that the total energy of the two tunnel-coupled wells is represented by the total Hamiltonian  $\hat{H}$ ,

$$\hat{H} = \begin{pmatrix} \varepsilon_L & T \\ T^* & \varepsilon_R \end{pmatrix}. \quad (3.38)$$

If we measure the energy, the possible outcomes are the eigenvalues of the corresponding observable, that is the total Hamiltonian  $\hat{H}$ . We therefore have to find the two eigenvectors  $|i\rangle$  and eigenvalues  $\varepsilon_i$  of  $\hat{H}$ , that is the solutions of

$$\hat{H}|i\rangle = \varepsilon_i|i\rangle, \quad i = 1, 2. \quad (3.39)$$

The result is

$$\begin{aligned} |1\rangle &= \frac{1}{N_1} [-2T|L\rangle + (\Delta + \varepsilon)|R\rangle], \quad \varepsilon_1 = \frac{1}{2}(\varepsilon_L + \varepsilon_R - \Delta) \\ |2\rangle &= \frac{1}{N_2} [2T|L\rangle + (\Delta - \varepsilon)|R\rangle], \quad \varepsilon_2 = \frac{1}{2}(\varepsilon_L + \varepsilon_R + \Delta) \\ \varepsilon &:= \varepsilon_L - \varepsilon_R, \quad \Delta := \varepsilon_2 - \varepsilon_1 = \sqrt{\varepsilon^2 + 4|T|^2} \\ N_{1,2} &:= \sqrt{4|T|^2 + (\Delta \pm \varepsilon)^2}. \end{aligned} \quad (3.40)$$

Discussion:

1. The eigenvectors  $|1\rangle$  and  $|2\rangle$  form a new orthonormal basis of the Hilbert space  $\mathcal{H} = C^2$  (the  $N_{1,2}$  are normalization factors).
2. The **level splitting**  $\Delta$  gives the energy difference between the new eigenenergies. It increases with increasing  $|T|$ .

3. For  $\varepsilon = 0$ , we find

$$\begin{aligned} |1\rangle &= \frac{1}{\sqrt{2}} [-(T/|T|)|L\rangle + |R\rangle] \\ |2\rangle &= \frac{1}{\sqrt{2}} [(T/|T|)|L\rangle + |R\rangle]. \end{aligned} \quad (3.41)$$

Remember that  $T$  is a complex quantity. If we chose  $T$  **real and negative**, i.e.  $T = -|T|$ , we find

$$\begin{aligned} \varepsilon_L = \varepsilon_R =: \varepsilon_0, \quad T = -|T| \rightsquigarrow |1\rangle &= \frac{1}{\sqrt{2}} [|L\rangle + |R\rangle], \quad \varepsilon_1 = \varepsilon_0 - |T| \\ |2\rangle &= \frac{1}{\sqrt{2}} [-|L\rangle + |R\rangle], \quad \varepsilon_2 = \varepsilon_0 + |T|. \end{aligned} \quad (3.42)$$

In particular, the symmetric linear combination  $|1\rangle$  now has a lower energy than the anti-symmetric combination  $|2\rangle$ : this is what we had found in the original double quantum well problem.

### 3.4.2 Energy Measurement in the Two-Level System

The measurement of the total energy is a bit more complicated to do in practice than the position measurement. For example, one can irradiate the system with light and measure an absorption peak when the photon energy  $h\nu$  matches the energy difference  $\Delta$  of the two levels. After the absorption, the particle is in the excited state  $|2\rangle$  with energy  $\varepsilon_2$ , before it was in its ground state  $|1\rangle$  with energy  $\varepsilon_1$ . The particle can go back into its ground state by, for example, spontaneous emission of another photon of energy  $\Delta$ .

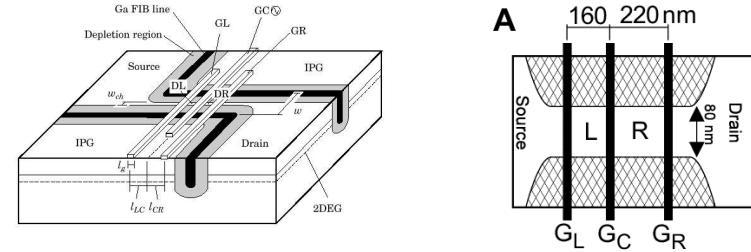
What we would like to find out now is the following: *where* is the particle, if it is in its ground state  $|1\rangle$  or its excited state  $|2\rangle$ ? For example, after we perform the absorption experiment and know that the particle is in its excited state, we would like to find out if it is in the left or in the right well. This means, we again perform a ‘position’ measurement, and we can apply exactly the same argument as before. The state before the position measurement is now the excited state

$$\begin{aligned} |2\rangle &= \frac{1}{N_2} [2T|L\rangle + (\Delta - \varepsilon)|R\rangle], \quad \varepsilon := \varepsilon_L - \varepsilon_R, \quad \Delta := \sqrt{\varepsilon^2 + 4|T|^2} \\ N_2 &:= \sqrt{4|T|^2 + (\Delta - \varepsilon)^2}. \end{aligned} \quad (3.43)$$

Comparing the coefficients in front of the basis vectors  $|L\rangle$  and  $|R\rangle$ , we recognize:

$$\begin{aligned} |c_0|^2 = p_0 &= \frac{4|T|^2}{4|T|^2 + (\Delta - \varepsilon)^2} = \begin{array}{l} \text{the probability to find the particle in the} \\ \text{left well after it was in the energy eigen-} \\ \text{state } |2\rangle. \end{array} \\ |c_1|^2 = p_1 &= \frac{(\Delta - \varepsilon)^2}{4|T|^2 + (\Delta - \varepsilon)^2} = \begin{array}{l} \text{the probability to find the particle in the} \\ \text{right well after it was in the energy eigen-} \\ \text{state } |2\rangle. \end{array} \end{aligned}$$

Again,  $p_0 + p_1 = |c_0|^2 + |c_1|^2 = 1$  as it must be. This means: we can *calculate* in advance the probability to find the particle in the left well after the absorption measurement, but we can’t tell *where* it is. If we know that the particle is in its excited state  $|2\rangle$ , but we haven’t done the



**Fig. 3.4: Left:** Schematic diagram of a ‘double gate single electron transistor’ (double quantum dot) by Fujisawa and Tarucha (1997). The 2DEG is located 100 nm below the surface of an AlGaAs/GaAs modulation-doped heterostructure with mobility  $8 \cdot 10^5 \text{ cm}^2 (\text{Vs})^{-1}$  and carrier concentration  $3 \cdot 10^{11} \text{ cm}^{-2}$  at 1.6 K in the dark and ungated. Ga focused ion beam implanted in-plane gates and Schottky gates define the dot system. A double dot is formed by applying negative gate voltages to the gates GL, GC, and GR. The structure can also be used for single-dot experiments, where negative voltages are applied to GL and GC only.

**Right:** Top view of the double quantum dot. Transport of electrons is through the narrow channel that connects source and drain. The gates themselves have widths of 40 nm. The two quantum dots contain approximately 15 (Left, L) and 25 (Right, R) electrons. The charging energies are 4 meV (L) and 1 meV (R), the energy spacing for single particle states in both dots is approximately 0.5 meV (L) and 0.25 meV (R).

position measurement yet, we still don’t know if the particle is in the right or in the left well. Its state  $|2\rangle$  has components both in the left and the right well. For example, if  $\varepsilon = 0$ , we find

$$\varepsilon = 0 \rightsquigarrow p_0 = p_1 = \frac{1}{2}. \quad (3.44)$$

In this case ‘it is completely unclear’ where the particle is. Only the subsequent position measurement can give us the answer: right with probability  $p_1 = 1/2$ , and left with probability  $p_0 = 1/2$ . On the other hand, if the coupling between the two wells is zero (in the case of an infinitely high barrier), we have  $T = 0$ . Then,

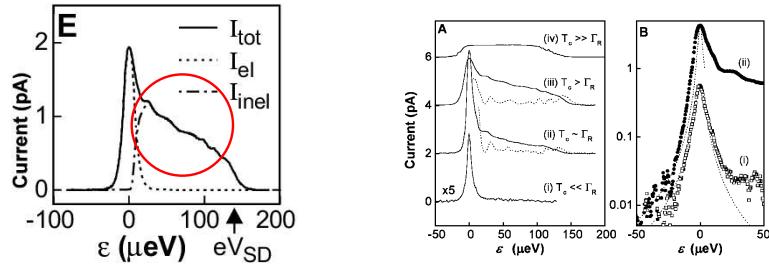
$$T = 0 \rightsquigarrow p_0 = 0, \quad p_1 = 1, \quad (3.45)$$

which means that the particle is with certainty in the right well. This is obvious because for  $T = 0$ , the energy eigenstate  $|2\rangle = |R\rangle$  is simply the basis vector  $|R\rangle$  corresponding to the particle in the right well with probability one.

### 3.4.3 \*Experiments in Double Quantum Dots

We now shortly describe of a recent experimental realization of a two-level system in a semiconductor structure. This experiment has been performed in coupled *artificial* atoms, that is coupled quantum dots, by Fujisawa and co-workers at the Technical University of Delft (Netherlands) in 1998.

The double quantum dot is realized in a 2DEG AlGaAs–GaAs semiconductor heterostructure, see Fig.(3.4). Focused ion beam implanted in-plane gates define a narrow channel of



**Fig. 3.5: Left:** Current at temperature  $T = 23\text{mK}$  as a function of the energy difference  $\varepsilon = \varepsilon_L - \varepsilon_R$  in the experiment by Fujisawa and co-workers. The total measured current is decomposed into an elastic and an inelastic component. If the difference  $\varepsilon$  between left and right dot energies  $\varepsilon_L$  and  $\varepsilon_R$  is larger than the source–drain–voltage, tunneling is no longer possible and the current drops to zero. The red circle marks the region of spontaneous emission of phonons. Phonons are the quanta of the lattice vibrations of the substrate (the whole semiconductor structure), in the same way as photons are the quanta of the electromagnetic (light) field. The spontaneous emission is characterized by the large ‘shoulder’ for  $\varepsilon > 0$  with an oscillation-like structure on top of it.

**Right:** The curves for the current for different values of the coupling  $T_c$  between the dots and the rate  $\Gamma_R$  for tunneling out into the drain region. The dotted curves are the negative derivatives of the currents with respect to energy  $\varepsilon$  to enhance the structure on the emission side of the current. **B** shows curves (i) and (ii) from A in a double-logarithmic plot, where the dashed lines are Lorentzian fits.

tunable width which connects source and drain (left and right electron reservoir). On top of it, three Schottky gates define tunable tunnel barriers for electrons moving through the channel. By applying negative voltages to the left, central, and right Schottky gate, two quantum dots (left  $L$  and right  $R$ ) are defined which are coupled to each other and to the source and to the drain. The tunneling of electrons through the structure is large enough to detect current but small enough to have a well-defined number of electrons ( $\sim 15$  and  $\sim 25$ ) on the left and the right dot, respectively. The Coulomb charging energy ( $\sim 4$  meV and  $\sim 1$  meV) for putting an additional electron onto the dots is the largest energy scale, see Fig.(3.4). By tuning simultaneously the gate voltages of the left and the right gate while keeping the central gate voltage constant, the double dot switches between the three states  $|0\rangle = |N_L, N_R\rangle$ ,  $|L\rangle = |N_L + 1, N_R\rangle$ , and  $|R\rangle = |N_L, N_R + 1\rangle$  with only *one additional electron* either in the left or in the right dot (see the following section, where the model is explained in detail).

The main experimental trick is to keep the system within these states and to change only the energy difference  $\varepsilon = \varepsilon_L - \varepsilon_R$  of the dots without changing too much, e.g., the barrier transmissions. The measured average spacing between single-particle states ( $\sim 0.5$  and  $\sim 0.25$  meV) is still a large energy scale compared to the scale on which  $\varepsilon$  is varied. The largest value of  $\varepsilon$  is determined by the source–drain voltage which is around  $0.14$  meV. The main findings are the following:

1. At a low temperature of  $23$  mK, the stationary tunnel current  $I$  as a function of  $\varepsilon$  shows a peak at  $\varepsilon = 0$  with a broad shoulder for  $\varepsilon > 0$  that oscillates on a scale of  $\approx 20 - 30\mu\text{eV}$ , see Fig.(3.5).

2. For larger temperatures  $T$ , the current increases stronger on the absorption side  $\varepsilon < 0$

than on the emission side. The data for larger  $T$  can be reconstructed from the  $23$  mK data by multiplication with Einstein–Bose factors (the Planck radiation law) for emission and absorption.

3. The energy dependence of the current on the emission side is between  $1/\varepsilon$  and  $1/\varepsilon^2$ . For larger distance of the left and right barrier ( $600$  nm on a surface gate sample instead of  $380$  nm for a focused ion beam sample), the period of the oscillations on the emission side appears to become shorter.

Those who are interested in more details on this fascinating experiment can read the article: T. Fujisawa, T. H. Oosterkamp, W. G. van der Wiel, B. W. Broer, R. Aguado, S. Tarucha, and L. P. Kouwenhoven, *Science* **282**, 932 (1998).

### 3.4.4 Energy Measurement in a Quantum Well

Consider the operator  $\hat{H}$ , the energy operator (Hamiltonian) for the infinite potential well with the eigenstates  $\psi_n$ , Eq.(3.6),

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad E_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2}, \quad n = 1, 2, 3, \dots$$

If the state  $\psi$  before the measurement is an eigenstate  $\psi = \psi_n$ , measurement of the energy yields the value  $E_n$  with probability  $|\langle \psi | \psi_n \rangle|^2$ , that is with probability 1, and other values  $E_m$ ,  $m \neq n$ , with probability  $|\langle \psi | \psi_m \rangle|^2 = |\langle \psi_n | \psi_m \rangle|^2 = 0$ . If the state  $\psi$  before the measurement is (cp. the problems)

$$\psi(x) = \sqrt{30/L} L^2 x(L-x) = \sum_{n=1}^{\infty} c_n \psi_n, \quad c_n = 2\sqrt{60} \frac{1 - (-1)^n}{n^3 \pi^3},$$

the probability to obtain the value  $E_n$  when measuring the energy is

$$\text{prob}(E_n) = |c_n|^2 = \begin{cases} 16 \cdot 60 / (n^6 \pi^6) & n \text{ odd} \\ 0 & n \text{ even} \end{cases}$$

In particular, we easily check (cp. the problems) that

$$\sum_{n=0}^{\infty} \text{prob}(E_n) = [n = 2k + 1] = \sum_{k=1}^{\infty} \frac{16 \cdot 60}{(2k + 1)^6 \pi^6} = 1$$

as it must be.

## 3.5 The Two-Level System: Time-Evolution

This section concludes our discussion of the two-level system, the simplest quantum mechanical system. Here, we discuss how the particle in the double well potential behaves as a function of time. As in the previous section, no new concepts are introduced here. We rather apply our formalism and our knowledge in order to become familiar with the axioms introduced above and the interpretation of states etc.

## 3.5.1 Time Evolution of States

To start with, we simply recall our first axiom of quantum mechanics here:

**Axiom 1:** A quantum mechanical system is described by a vector  $|\Psi(t)\rangle \equiv \Psi(t)$  of a Hilbert space  $\mathcal{H}$ . The time evolution of  $\Psi(t)$  is determined by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = \hat{H} \Psi(t) \quad (3.46)$$

The Hamilton operator  $\hat{H}$  is an operator corresponding to the total energy of the system. The solutions of the stationary Schrödinger equation at fixed energy,

$$\hat{H}\phi = E\phi \quad (3.47)$$

are called **stationary states**, the possible energies  $E$  eigenenergies.

We now specialize everything to our two-level system:

Hilbert space	$\mathcal{H} = C^2$	2d complex vector space
Basis vectors	$ L\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix},  R\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$	particle left or right
Arbitrary vector	$ \psi\rangle = c_0 L\rangle + c_1 R\rangle,  c_0 ^2 +  c_1 ^2 = 1$	particle in arbitrary state
Hamiltonian	$\hat{H} = \begin{pmatrix} \varepsilon_L & T \\ T^* & \varepsilon_R \end{pmatrix}$	two-dimensional matrix
Stationary states	$\hat{H} 1\rangle = \varepsilon_1 1\rangle, \hat{H} 2\rangle = \varepsilon_2 2\rangle$	The two energy eigenstates

**Time evolution** means the following: Suppose the state of the quantum system at time  $t = 0$  is  $|\Psi(t=0)\rangle = |\Psi_0\rangle$ . Then, the solution of the time-dependent Schrödinger equation  $i\hbar \partial_t \Psi(t) = \hat{H} \Psi(t)$  gives us the state  $|\Psi(t)\rangle$  at a later time  $t > 0$ .

CASE 1: Time evolution of a stationary state

If the initial state  $|\Psi_0\rangle$  is a stationary state, the time-evolution is simple:

$$\begin{aligned} |\Psi(t=0)\rangle &= |1\rangle \rightsquigarrow |\Psi(t>0)\rangle = |1\rangle e^{-i\varepsilon_1 t/\hbar} \\ |\Psi(t=0)\rangle &= |2\rangle \rightsquigarrow |\Psi(t>0)\rangle = |2\rangle e^{-i\varepsilon_2 t/\hbar} \end{aligned} \quad (3.48)$$

because

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t} [1] e^{-i\varepsilon_1 t/\hbar} = \underline{\varepsilon_1 |1\rangle} e^{-i\varepsilon_1 t/\hbar} = \hat{H}|1\rangle e^{-i\varepsilon_1 t/\hbar} = \hat{H}|\Psi(t)\rangle. \quad (3.49)$$

(the same for  $|\Psi(t=0)\rangle = |2\rangle$ ). The time-evolution is ‘trivial’ and just given by the phase factor  $e^{-iEt/\hbar}$ , where  $E$  is the eigenenergy of the stationary state.

CASE 2: Time evolution of a superposition of the two energy eigenstates

$$|\Psi(t=0)\rangle = \alpha_1|1\rangle + \alpha_2|2\rangle \rightsquigarrow |\Psi(t)\rangle = \alpha_1|1\rangle e^{-i\varepsilon_1 t/\hbar} + \alpha_2|2\rangle e^{-i\varepsilon_2 t/\hbar} \quad (3.50)$$

because

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle &= i\hbar \frac{\partial}{\partial t} [\alpha_1|1\rangle e^{-i\varepsilon_1 t/\hbar} + \alpha_2|2\rangle e^{-i\varepsilon_2 t/\hbar}] \\ &= \alpha_1 \varepsilon_1 |1\rangle e^{-i\varepsilon_1 t/\hbar} + \alpha_2 \varepsilon_2 |2\rangle e^{-i\varepsilon_2 t/\hbar} \\ &= \hat{H} \alpha_1 |1\rangle e^{-i\varepsilon_1 t/\hbar} + \hat{H} \alpha_2 |2\rangle e^{-i\varepsilon_2 t/\hbar} = \hat{H} |\Psi(t)\rangle. \end{aligned} \quad (3.51)$$

To obtain the time evolution of an arbitrary initial state  $|\Psi(t=0)\rangle$ , we therefore have to do the following: decompose  $|\Psi(t=0)\rangle$  into a linear combination of energy eigenstates ( $|1\rangle$  and  $|2\rangle$ ). Then, simply dress the stationary states in this linear combination with the phase factors  $e^{-i\varepsilon_1 t/\hbar}$  and  $e^{-i\varepsilon_2 t/\hbar}$ . The linearity of the Schrödinger equation makes it that simple: the time evolution of a sum of stationary states is the sum of the time-evolved linear components of this sum.

The calculational effort is in the determination of the coefficients  $\alpha_1$  and  $\alpha_2$ : we discuss this in the special

CASE 3: The initial state is  $|\Psi(t=0)\rangle = |L\rangle$ , describing the particle in the left well. Note that we don’t have simply a time evolution given by a phase factor:

$$|\Psi(t=0)\rangle = |L\rangle \rightsquigarrow |\Psi(t>0)\rangle \neq e^{-iEt/\hbar} |L\rangle \quad \text{for some } E.$$

The state  $|L\rangle$  is not an eigenstate of the Hamiltonian  $\hat{H}$ , therefore its time evolution is not given by a simple phase factor. What we have to do is clear: we have to find the decomposition of the vector  $|L\rangle$  into a linear combination of energy eigenstates  $|1\rangle$  and  $|2\rangle$ ,

$$|\Psi(t=0)\rangle = |L\rangle = \alpha_1|1\rangle + \alpha_2|2\rangle \rightsquigarrow |\Psi(t)\rangle = \alpha_1|1\rangle e^{-i\varepsilon_1 t/\hbar} + \alpha_2|2\rangle e^{-i\varepsilon_2 t/\hbar}. \quad (3.52)$$

For simplicity, we do this for the special case of negative  $T$  and identical energy parameters  $\varepsilon_L = \varepsilon_R$  in the Hamiltonian  $\hat{H}$ . We had calculated already before in (3.41),

$$\begin{aligned} \varepsilon_L = \varepsilon_R =: \varepsilon_0, \quad T = -|T| \rightsquigarrow |1\rangle &= \frac{1}{\sqrt{2}} [|L\rangle + |R\rangle], \quad \varepsilon_1 = \varepsilon_0 - |T| \\ |2\rangle &= \frac{1}{\sqrt{2}} [-|L\rangle + |R\rangle], \quad \varepsilon_2 = \varepsilon_0 + |T|. \end{aligned} \quad (3.53)$$

We solve this equation for  $|L\rangle$ ,

$$|L\rangle = \frac{1}{\sqrt{2}} [|1\rangle - |2\rangle] \rightsquigarrow \alpha_1 = \frac{1}{\sqrt{2}}, \quad \alpha_2 = -\frac{1}{\sqrt{2}}. \quad (3.54)$$

By this we have found our desired result, that is the time evolution of the initial state  $|L\rangle$ ,

$$|\Psi(t=0)\rangle = |L\rangle \rightsquigarrow |\Psi(t)\rangle = \frac{1}{\sqrt{2}} [|1\rangle e^{-i\varepsilon_1 t/\hbar} - |2\rangle e^{-i\varepsilon_2 t/\hbar}]. \quad (3.55)$$

We have expressed  $|\Psi(t)\rangle$  in the basis of the energy eigenstates  $|1\rangle$  and  $|2\rangle$ . We now would like to express  $|\Psi(t)\rangle$  in the basis of the left and right states,  $|L\rangle$  and  $|R\rangle$ : this is simple because we know

$$\begin{aligned} |1\rangle &= \frac{1}{\sqrt{2}} [|L\rangle + |R\rangle], \quad |2\rangle = \frac{1}{\sqrt{2}} [-|L\rangle + |R\rangle] \\ \rightsquigarrow |\underline{\Psi(t)}\rangle &= \frac{1}{\sqrt{2}} [|1\rangle e^{-i\varepsilon_1 t/\hbar} - |2\rangle e^{-i\varepsilon_2 t/\hbar}] = \\ &= \frac{1}{2} \{ [|L\rangle + |R\rangle] e^{-i\varepsilon_1 t/\hbar} - [-|L\rangle + |R\rangle] e^{-i\varepsilon_2 t/\hbar} \} = \\ &= \frac{1}{2} \{ |L\rangle [e^{-i\varepsilon_1 t/\hbar} + e^{-i\varepsilon_2 t/\hbar}] + |R\rangle [e^{-i\varepsilon_1 t/\hbar} - e^{-i\varepsilon_2 t/\hbar}] \} \\ &=: \underline{c_0(t)|L\rangle + c_1(t)|R\rangle} \\ c_0(t) &:= \frac{1}{2} [e^{-i\varepsilon_1 t/\hbar} + e^{-i\varepsilon_2 t/\hbar}], \quad c_1(t) := \frac{1}{2} [e^{-i\varepsilon_1 t/\hbar} - e^{-i\varepsilon_2 t/\hbar}]. \end{aligned} \quad (3.56)$$

The coefficients  $c_0(t)$  and  $c_1(t)$  have a clear physical meaning: let us recall

$$\begin{aligned} |c_0|^2(t) = p_0(t) &= \text{the probability to find the particle in the left well} \\ |c_1|^2(t) = p_1(t) &= \text{the probability to find the particle in the right well.} \end{aligned} \quad (3.57)$$

Obviously, these probabilities are a function of time now:  $|\Psi(t)\rangle$  is **not stationary**. We calculate

$$\begin{aligned} p_0(t) &= \frac{1}{4} |e^{-i\varepsilon_1 t/\hbar} + e^{-i\varepsilon_2 t/\hbar}|^2 = \frac{1}{2} \{1 + \cos[(\varepsilon_1 - \varepsilon_2)t/\hbar]\} \\ &= \cos^2\left[\frac{(\varepsilon_1 - \varepsilon_2)t}{2\hbar}\right] \\ p_1(t) &= \frac{1}{4} |e^{-i\varepsilon_1 t/\hbar} - e^{-i\varepsilon_2 t/\hbar}|^2 = \frac{1}{2} \{1 - \cos[(\varepsilon_1 - \varepsilon_2)t/\hbar]\} \\ &= \sin^2\left[\frac{(\varepsilon_1 - \varepsilon_2)t}{2\hbar}\right] \end{aligned} \quad (3.58)$$

and therefore

$$\begin{aligned} \cos^2\left[\frac{(\varepsilon_1 - \varepsilon_2)t}{2\hbar}\right] &= \text{the probability to find the particle in the left well} \\ \sin^2\left[\frac{(\varepsilon_1 - \varepsilon_2)t}{2\hbar}\right] &= \text{the probability to find the particle in the right well.} \end{aligned} \quad (3.59)$$

As a function of time, the probabilities oscillate with an angular frequency that is given by the **energy splitting**  $\Delta = \varepsilon_2 - \varepsilon_1 = 2|T|$ , divided by  $\hbar$ . At the initial time  $t = 0$ , the particle is in the left well (the probability  $p_0(0) = 1$ ), but for  $t > 0$  this probability starts to oscillate: the particle tunnels from the left well into the right well, back into the left well and so forth.

## 4. IMPORTANT QUANTUM MECHANICAL MODEL SYSTEMS

### 4.1 The Harmonic Oscillator I

#### 4.1.1 Model

The one-dimensional harmonic oscillator is defined by a **quadratic potential**  $V(x)$  that for convenience is chosen to be symmetric to the origin,

$$V(x) = \frac{1}{2}m\omega^2 x^2. \quad (4.1)$$

Here,  $m$  is the mass of the particle and  $\omega$  the parameter that determines the shape of the parabola. We wish to determine the behaviour of a particle of mass  $m$  in this potential. In classical (Newtonian) physics, all one would have to do would be to solve Newton's equations for a given initial position  $x_0$  and a given initial momentum  $p_0$  at time  $t = 0$  to determine  $x(t)$  and  $p(t)$  at a later time  $t > 0$ . The total energy

$$E = \frac{p^2}{2m} + V(x) = \frac{p_0^2}{2m} + V(x_0) \quad (4.2)$$

is constant and determines an ellipse in phase space. The particle starts at the point  $(x_0, p_0)$  on this ellipse and then moves on this ellipse. Of course, as a function of time  $t$  we can easily solve for  $x(t)$  by solving the differential equation (Newton's law)  $m\ddot{x} = F(x) = -V'(x) = -m\omega^2 x$ .

In quantum mechanics, we have the total energy replaces by the Hamilton operator (Hamiltonian)

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2, \quad (4.3)$$

and we have to solve the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \hat{H} \Psi(x, t) \quad (4.4)$$

for a given initial wave function  $\Psi(x, 0)$ . We have learned that this can be achieved by first solving the stationary Schrödinger equation

$$\hat{H}\psi = E\psi \rightsquigarrow \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\right) \psi(x) = E\psi(x), \quad (4.5)$$

which is an equation for the possible energy eigenvalues  $E$  and eigenfunctions  $\psi(x)$ . The eigenfunctions are useful themselves as they provide inside into the possible states the particle can be in. We have also learned that the eigenfunctions provide a basis into which the initial wave function  $\Psi(x)$  can be expanded and thus the time-evolution of an arbitrary initial wave function can be obtained.

## 4.1.2 Solution of the Differential Equation

Now we actually want to solve (4.5). We introduce dimensionless quantities

$$q := \sqrt{\frac{m\omega}{\hbar}}x, \quad \varepsilon := \frac{E}{\hbar\omega}, \quad \phi(q) := \psi(x). \quad (4.6)$$

Then, (4.5) becomes

$$\phi''(q) + (2\varepsilon - q^2)\phi(q) = 0. \quad (4.7)$$

For large  $q \rightarrow \infty$ , one can neglect the term  $\propto \varepsilon$ . This yields the asymptotic behaviour of  $\phi(q \rightarrow \pm\infty)$ ,

$$\phi(q \rightarrow \pm\infty) \propto e^{\pm q^2/2}, \quad (4.8)$$

which you can check by differentiating

$$\phi'(q \rightarrow \pm\infty) \propto \pm q e^{\pm q^2/2}, \quad \phi''(q \rightarrow \pm\infty) \propto \pm e^{\pm q^2/2} + q^2 e^{\pm q^2/2} \rightarrow q^2 e^{\pm q^2/2}. \quad (4.9)$$

This roughly is an example of how an **asymptotic analysis** of a differential equation is performed; if you are interested for more mathematical details of the interesting theory of asymptotic analysis have a look at the book by Bender and Orszag.

We obviously have two different solutions: one grows to infinity as  $q \rightarrow \pm\infty$ , while the other goes to zero. Wave functions have to be normalized which is impossible for the solution that grows to infinity. We exclude that solution and write  $\phi(q)$  as

$$\phi(q) = e^{-q^2/2}h(q), \quad (4.10)$$

which is an **ANSATZ** with an up to now unknown function  $h(q)$  that we wish to determine. To do so, we plug it into our differential equation (4.7) and use

$$\begin{aligned} \phi'(q) &= -qe^{-q^2/2}h(q) + e^{-q^2/2}h'(q) \\ \phi''(q) &= -e^{-q^2/2}h(q) + q^2e^{-q^2/2}h(q) - 2qe^{-q^2/2}h'(q) + e^{-q^2/2}h''(q), \end{aligned} \quad (4.11)$$

which leads to

$$h''(q) - 2qh'(q) + (2\varepsilon - 1)h(q) = 0. \quad (4.12)$$

We try to solve this by a **power series**

$$\begin{aligned} h(q) &= \sum_{k=0}^{\infty} a_k q^k, \quad h'(q) = \sum_{k=0}^{\infty} k a_k q^{k-1} \\ h''(q) &= \sum_{k=2}^{\infty} k(k-1)a_k q^{k-2} = \sum_{k=0}^{\infty} (k+1)(k+2)a_{k+2} q^k. \end{aligned} \quad (4.13)$$

We insert these series into (4.12),

$$\sum_{k=0}^{\infty} [(k+1)(k+2)a_{k+2} - 2ka_k + (2\varepsilon - 1)a_k] q^k = 0. \quad (4.14)$$

The left side of the equation must be zero for any value of  $q$  which can only be true if all the coefficients in [...] vanish. The powers  $q^k$  form an infinite basis  $q^0, q^1, q^2, q^3, \dots$ ; if any function expanded in this basis is zero, all expansion coefficients must be zero. From [...] = 0 in (4.14), we therefore have

$$a_{k+2} = \frac{2k - 2\varepsilon + 1}{(k+1)(k+2)} a_k. \quad (4.15)$$

This is a recursion relation for the coefficients  $a_k$ . For large  $k \rightarrow \infty$ , one has

$$a_{k+2} \approx \frac{2}{k} a_k, \quad k \rightarrow \infty, \quad (4.16)$$

unless the  $a_k$  become zero above some  $k = n$ . The infinite power series  $h(q)$  becomes asymptotical equal to the exponential function  $e^{q^2}$  for large  $q$ : consider

$$e^{q^2} = \sum_j \frac{q^{2j}}{j!} \rightsquigarrow [k = 2j \text{ even}] \frac{a_{k+2}}{a_k} = \frac{(k/2)!}{(k/2+1)!} = \frac{1}{k/2+1} \rightarrow \frac{2}{k}, \quad k \rightarrow \infty. \quad (4.17)$$

Now, this is obviously not what we had intended with our Ansatz, because this would mean that the wave function  $\phi(q) = e^{-q^2/2}h(q) \rightarrow e^{q^2/2}$  which means that it is no longer normalizable. The only possibility for a solution  $\phi(q)$  that vanishes as  $q \rightarrow \pm\infty$  therefore is obtained by demanding that the  $a_k$  become *zero* above some  $n = k$  whence  $h(q)$  becomes a polynomial of finite degree. For this to be the case, the numerator in (4.15) has to vanish for some  $k = n$  which means

$$2\varepsilon = 2n + 1 \rightsquigarrow \varepsilon \equiv \varepsilon_n = n + \frac{1}{2}. \quad (4.18)$$

The possible energy values  $E$  are therefore

$$E \equiv E_n = \hbar\omega \left( n + \frac{1}{2} \right), \quad n = 0, 1, 2, 3, \dots \quad (4.19)$$

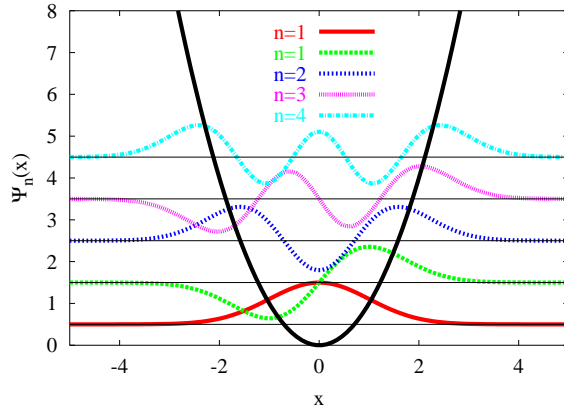
This is the famous quantization of the energy of the harmonic oscillator, which Planck had postulated to explain the blackbody radiation in 1900!

For each non-negative integer  $n$  we obtain one energy eigenvalue and the corresponding eigenfunction  $\phi_n(q) = h_n(q)e^{-q^2/2}$  from the finite recursion formula (4.15) for the polynomial  $h_n(q)$ . Here, we already use the index  $n$  to denote the  $n$ -th solution. The polynomials  $h(q)$  fulfill the differential equation (4.12) with  $2\varepsilon = n$ , that is

$$h''(q) - 2qh'(q) + 2nh(q) = 0. \quad (4.20)$$

The polynomials  $h_n(q)$  that fulfill (4.20) are called **Hermite polynomials**  $H_n(q)$  if they are normalized such that the wavefunctions  $\psi_n(x) = \phi_n(q)$  are normalized: the result for the normalized eigenfunctions  $\psi_n(x)$  with eigenenergy  $E_n$ , that is the solutions of (4.5), is

$$\boxed{\begin{aligned} \psi_n(x) &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{n!2^n}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega}{2\hbar}x^2} \\ H_n(q) &= (-1)^n e^{q^2} \frac{d^n}{dq^n} e^{-q^2}. \end{aligned}} \quad (4.21)$$



**Fig. 4.1:** Lowest eigenstate wave functions  $\psi_n(x)$ , Eq.(4.21) of the one-dimensional harmonic oscillator potential  $V(x) = (1/2)m\omega^2x^2$  (black curve). Wave functions are in units  $(m\omega/\pi\hbar)^{1/4}$ . The curves have an offset for clarity.

We do not prove the explicit form of the Hermite polynomials here; in the next section we will learn an alternative method to calculate the  $E_n$  and the  $\psi_n(x)$  anyway. Here, we calculate  $H_n(x)$  for the first  $n$ , using (4.21) (denote  $q$  by  $x$  here)

$$\begin{aligned} H_0(x) &= 1 \\ H_1(x) &= 2x \\ H_2(x) &= 4x^2 - 2 \\ H_3(x) &= 8x^3 - 12x \\ H_4(x) &= 16x^4 - 48x^2 + 12. \end{aligned} \quad (4.22)$$

The lowest eigenfunctions  $\psi_n(x)$  are shown in Fig. (4.1).

## 4.2 The Harmonic Oscillator II

We discuss our results for the eigenfunctions and energy eigenvalues of the **harmonic oscillator**,

$$\begin{aligned} \psi_n(x) &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{n!2^n}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega}{2\hbar}x^2} \\ E_n &= \hbar\omega\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, 3, \dots \end{aligned} \quad (4.23)$$

It is very instructive to compare it with our results for the eigenfunctions and eigenenergies of the **infinite well potential**,

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad \varepsilon_n = \frac{n^2\hbar^2\pi^2}{2mL^2}, \quad n = 1, 2, 3, \dots \quad (4.24)$$

### 4.2.1 The Hilbert space of wave functions

#### Infinite Well Hilbert Space

Let us recall what we know from the infinite potential well:

The eigen functions  $\phi_n(x)$  of the infinite potential well form the basis of a **linear vector space**  $\mathcal{H}_{well}$  of functions  $f(x)$  defined on the interval  $[0, L]$  with  $f(0) = f(L) = 0$ . The  $\phi_n(x)$  form an orthonormal basis:

$$\int_0^L dx |\phi_n(x)|^2 = 1, \quad \int_0^L dx \phi_n^*(x) \phi_m(x) = \delta_{nm}. \quad (4.25)$$

(We can omit the  $*$  here because the  $\phi_n$  are real). Note that the orthonormal basis is of infinite dimension because there are infinitely many  $n$ . The infinite dimension of the vector space (function space)  $\mathcal{H}_{well}$  is the main difference to ordinary, finite dimensional vector spaces like the  $R^3$ . Any function  $f(x) \in \mathcal{H}_{well}$  (like any arbitrary vector in, e.g., the vector space  $R^3$ ) can be expanded into a linear combination of basis 'vectors', i.e. eigen functions  $\phi_n(x)$ :

$$f(x) = \sum_{n=1}^{\infty} c_n \phi_n(x), \quad c_n = \int_0^L dx f(x) \phi_n(x). \quad (4.26)$$

We start to count the eigenstates from  $n = 1$ .

#### Harmonic Oscillator Hilbert Space

For the harmonic oscillator, the situation is completely analogous. The difference now is that the potential is no longer the infinite well but a harmonic potential. The wave functions are not defined on the finite interval  $[0, L]$  but on the infinite interval  $[-\infty, \infty]$ .

The eigen functions  $\psi_n(x)$  of the harmonic oscillator form the basis of a **linear vector space**  $\mathcal{H}_{osc}$  of functions  $f(x)$  defined on the interval  $[-\infty, \infty]$  with  $f(-\infty) = f(\infty) = 0$ . The  $\psi_n(x)$  form an orthonormal basis:

$$\int_{-\infty}^{\infty} dx |\psi_n(x)|^2 = 1, \quad \int_{-\infty}^{\infty} dx \psi_n^*(x) \psi_m(x) = \delta_{nm}. \quad (4.27)$$

(We can omit the  $*$  here because the  $\psi_n$  are real). Note that the orthonormal basis is of infinite dimension because there are infinitely many  $n$ . The infinite dimension of the vector space (function space)  $\mathcal{H}_{osc}$  is the main difference to ordinary, finite dimensional vector spaces like the  $R^3$ . Any function  $f(x) \in \mathcal{H}_{osc}$  (like any arbitrary vector in, e.g., the vector space  $R^3$ ) can be expanded into a linear combination of basis 'vectors', i.e. eigen functions  $\psi_n(x)$ :

$$f(x) = \sum_{n=0}^{\infty} c_n \psi_n(x), \quad c_n = \int_{-\infty}^{\infty} dx f(x) \psi_n(x). \quad (4.28)$$

We start to count the eigenstates from  $n = 0$  and not  $n = 1$  as for the infinite well. To prove the orthogonality (4.27) is a bit more difficult for the harmonic oscillator than for the infinite potential well. It can be done by using the properties of the Hermite polynomials.

### Harmonic Oscillator: Parity

The harmonic oscillator functions have the symmetry property

$$\psi_n(x) = (-1)^n \psi_n(-x), \quad (4.29)$$

that is, they are symmetric or antisymmetric with respect to the symmetry point  $x = 0$  of the potential  $V(x)$ , in alternating order with the **quantum number**  $n$ . The lowest eigenstate  $\psi_0(x)$  is symmetric and has no node, the next eigenstate  $\psi_1(x)$  is anti-symmetric and has one node,  $\psi_2(x)$  is again symmetric and has two zeros, and so on.

### Infinite Well: Parity

The wave functions have the symmetry property

$$\phi_n(x + L/2) = (-1)^{n-1} \phi_n(L/2 - x), \quad (4.30)$$

that is they are symmetric or antisymmetric with respect to the symmetry point  $x = L/2$  of the infinite well potential  $V(x)$ , in alternating order with the **quantum number**  $n$ . The lowest eigenstate  $\phi_1(x)$  is symmetric and has no node, the next eigenstate  $\phi_2(x)$  is anti-symmetric and has one node,  $\phi_3(x)$  is again symmetric and has two zeros, and so on.

We recognize that conceptually, everything is really completely analogous (the counting from 0 or 1 is a matter of convention).

## 4.2.2 Discussion: Energy Eigenvalues

### Harmonic Oscillator Energies

The lowest energy eigenvalue of the harmonic oscillator is

$$E_0 = \frac{1}{2} \hbar \omega > 0. \quad (4.31)$$

This energy is *above* the bottom at  $x = 0$  of the potential  $V(x) = (1/2)m\omega^2 x^2$ .

### Infinite Well Energies

The lowest energy eigenvalue of the infinite potential well is

$$\varepsilon_1 = \frac{\hbar^2 \pi^2}{2mL^2} > 0. \quad (4.32)$$

This energy is *above* the bottom at  $x = 0$  of the infinite well potential (which is zero inside the infinite well).

According to our axiom 2c,

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**Axiom 2c:** The possible outcomes of measurements of the energy corresponding to the hermitian linear Hamilton operator  $\hat{H}$  are the eigenvalues of  $\hat{H}$ . Immediately after the measurement, the quantum system is in the eigenstate of  $\hat{H}$  corresponding to the eigenvalue that is measured.

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the lowest possible energy value that can be measured is  $(1/2)\hbar\omega$  for the linear harmonic oscillator. It is called **zero-point energy**.

## 4.2.3 Harmonic Oscillator: Expectation Values

We calculate the ground state expectation values

$$\langle 0|x^2|0\rangle = \int_{-\infty}^{\infty} dx x^2 |\Psi_0(x)|^2 = \sqrt{\frac{m\omega}{\pi\hbar}} \int_{-\infty}^{\infty} dx x^2 e^{-\frac{m\omega}{\hbar}x^2}. \quad (4.33)$$

This integral is evaluated using

$$\int_{-\infty}^{\infty} dx e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}, \quad \int_{-\infty}^{\infty} dx x^2 e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}} = -\frac{\partial}{\partial \alpha} \sqrt{\frac{\pi}{\alpha}} = \frac{1}{2\alpha} \sqrt{\frac{\pi}{\alpha}} \quad (4.34)$$

(integration by differentiation). Therefore,

$$\langle 0|x^2|0\rangle = \frac{1}{2} \frac{\hbar}{m\omega}. \quad (4.35)$$

Similarly,

$$\langle 0|p^2|0\rangle = -\hbar^2 \int_{-\infty}^{\infty} dx e^{-\frac{m\omega}{2\hbar}x^2} \frac{\partial^2}{\partial x^2} e^{-\frac{m\omega}{2\hbar}x^2} \sqrt{\frac{m\omega}{\pi\hbar}} = \hbar m\omega - m^2 \omega^2 \langle 0|x^2|0\rangle = \frac{1}{2} m\hbar\omega. \quad (4.36)$$

Using this, we can calculate the expectation value of the potential and the kinetic energy in the ground state,

$$\begin{aligned} \langle 0|E_{\text{kin}}|0\rangle &= \frac{1}{2m} \langle 0|p^2|0\rangle = \frac{1}{4} \hbar\omega \\ \langle 0|E_{\text{pot}}|0\rangle &= \frac{1}{2} m\omega^2 \langle 0|x^2|0\rangle = \frac{1}{4} \hbar\omega. \end{aligned} \quad (4.37)$$

Note that we have  $\langle 0|E_{\text{kin}}|0\rangle = \langle 0|E_{\text{pot}}|0\rangle$  (Virial theorem).

## 4.3 Ladder Operators, Phonons and Photons

In this section, we solve the one-dimensional harmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2, \quad (4.38)$$

with a powerful operator method that does not rely on complicated differential equation but on simple algebraic manipulations.

### 4.3.1 The Ladder Operators $a$ and $a^\dagger$

We define the two operators

$$a := \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + \frac{i}{\sqrt{2m\hbar\omega}} \hat{p}, \quad a^\dagger := \sqrt{\frac{m\omega}{2\hbar}} \hat{x} - \frac{i}{\sqrt{2m\hbar\omega}} \hat{p}. \quad (4.39)$$

You have showed in the problems that if two operators  $A$  and  $B$  are hermitian,  $A = A^\dagger$ ,  $B = B^\dagger$  the linear combination  $C := A + iB$  is not hermitian but  $C^\dagger = A - iB$  (remember the analogy to a complex number  $z = x + iy$ ,  $z^* = x - iy$ ). We know that  $\hat{x}$  and  $\hat{p}$  are hermitian,



therefore  $a^\dagger$  ('a dagger') is the hermitian conjugate of  $a$ . From the commutator of  $\hat{x}$  and  $\hat{p}$  we easily find (see the problems)

$$[\hat{x}, \hat{p}] = i\hbar \rightsquigarrow [a, a^\dagger] = 1. \quad (4.40)$$

We define the **number operator**

$$\hat{N} := a^\dagger a \quad (4.41)$$

which is a hermitian operator because  $\hat{N}^\dagger = (a^\dagger a)^\dagger = a^\dagger (a^\dagger)^\dagger = \hat{N}$ . The eigenvalues of  $\hat{N}$  must be real therefore. We denote the eigenvalues of  $\hat{N}$  by  $n$  and show that the  $n$  are non-negative integers: First, we denote the corresponding (normalized) eigenvectors of  $\hat{N}$  by  $|n\rangle$ ,

$$\hat{N}|n\rangle = n|n\rangle. \quad (4.42)$$

STEP 1: We show  $n \geq 0$ : remember the scalar product of two states  $|\psi\rangle$  and  $|\phi\rangle$  is denoted as  $\langle\phi|\psi\rangle$ .

$$0 \leq \|a|n\rangle\|^2 = \langle n|a^\dagger a|n\rangle = \langle n|\hat{N}|n\rangle = n\langle n|n\rangle = n. \quad (4.43)$$

STEP 2: We step down the ladder: if  $|n\rangle$  is an eigenvector of  $\hat{N}$  with eigenvalue  $n$ , then  $a|n\rangle$  is an eigenvector of  $\hat{N}$  with eigenvalue  $n-1$ ,  $a^2|n\rangle$  is an eigenvector of  $\hat{N}$  with eigenvalue  $n-2$ ,  $a^3|n\rangle$  is an eigenvector of  $\hat{N}$  with eigenvalue  $n-3, \dots$

$$\begin{aligned} \hat{N}a &= a^\dagger a a = (a a^\dagger - [a, a^\dagger]) a = (a a^\dagger - 1) a = a(\hat{N} - 1) \\ \rightsquigarrow \hat{N}a|n\rangle &= a(\hat{N} - 1)|n\rangle = (n-1)a|n\rangle \\ \rightsquigarrow \hat{N}a^2|n\rangle &= (\hat{N}a)a|n\rangle = a(\hat{N} - 1)a|n\rangle = a(n-1-1)a|n\rangle = (n-2)a^2|n\rangle \\ &\dots \end{aligned} \quad (4.44)$$

The state  $a|n\rangle$  is an eigenstate of  $\hat{N}$  with eigenvalue  $n-1$  and therefore must be proportional to  $|n-1\rangle$ ,

$$\begin{aligned} a|n\rangle &= C_n|n-1\rangle \rightsquigarrow n = \langle n a^\dagger a n | = |C_n|^2 \langle n-1|n-1\rangle = |C_n|^2 \\ \rightsquigarrow a|n\rangle &= \sqrt{n}|n-1\rangle. \end{aligned} \quad (4.45)$$

The operator  $a$  takes us from one eigenstate with eigenvalue  $n$  to a lower eigenstate with eigenvalue  $n-1$ .

STEP 3: We show that  $n$  must be an integer, and the only possible eigenstates of  $\hat{N}$  are  $|0\rangle, |1\rangle, |2\rangle, \dots$

If we step down the ladder to lower and lower eigenvalues, we eventually would come to negative eigenvalues which can't be because all eigenvalues of  $\hat{N}$  must be non-negative! The lowest possible eigenstate is  $a|1\rangle = |0\rangle$  with eigenvalue 0:

$$\begin{aligned} \hat{N}a|1\rangle &= (n-1)a|1\rangle \\ \rightsquigarrow \hat{N}a|1\rangle &= 0 \cdot a|1\rangle \end{aligned} \quad (4.46)$$

For any  $n$  with  $0 < n < 1$ , the eigenvalue equation  $\hat{N}a|n\rangle = (n-1)a|n\rangle$  can only be true if  $a|n\rangle = 0$  is the zero-vector. It then becomes the trivial equation  $0 = 0$  that contains no

contradictions. But  $a|n\rangle$  cannot be the zero-vector because the norm of  $a|n\rangle$  is  $\|a|n\rangle\| = \sqrt{n} > 0$ . Therefore,  $0 < n < 1$  leads to a contradiction. In the same way, there can't be values of  $n$  with  $1 < n < 2$  (application of  $a$  leads us to the case  $0 < n < 1$  which is already excluded). As a result,  **$n$  is an integer.**

Step 4: The normalized state  $a^\dagger|n\rangle$  is (the proof is left for the problems)

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \quad (4.47)$$

Therefore,  $a^\dagger$  takes us up the ladder from one eigenstate  $|n\rangle$  to the next higher  $|n+1\rangle$ . All the normalized eigenstates  $|n\rangle$  can be created from the ground state  $|0\rangle$  by successive application of the ladder operator  $a^\dagger$ :

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle. \quad (4.48)$$

#### 4.3.2 The Harmonic Oscillator

The connection of the above algebraic *tour de force* with the harmonic oscillator is very simple: The Hamiltonian (4.38) can be written as

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 = \hbar\omega \left( a^\dagger a + \frac{1}{2} \right) = \hbar\omega \left( \hat{N} + \frac{1}{2} \right) \quad (4.49)$$

which you can check by inserting the definitions of  $a$  and  $a^\dagger$ . The eigenvectors of  $\hat{H}$  are the eigenvectors of  $\hat{N}$ :

$$\hat{H}|n\rangle = \hbar\omega \left( \hat{N} + \frac{1}{2} \right) |n\rangle = \hbar\omega \left( n + \frac{1}{2} \right) |n\rangle, \quad (4.50)$$

from which we can read off the eigenvalues of the harmonic oscillator,  $E_n = \hbar\omega(n+1/2)$ . The corresponding eigenfunctions are, of course, the eigenfunctions of the harmonic oscillator,

$$|n\rangle \leftrightarrow \psi_n(x) = \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} \frac{1}{\sqrt{n!2^n}} H_n \left( \sqrt{\frac{m\omega}{\hbar}} x \right) e^{-\frac{m\omega}{2\hbar} x^2}. \quad (4.51)$$

This is not so easy to see directly; it is proofed for the ground state  $|0\rangle$  in the problems.

#### 4.3.3 Phonons and Photons

We call the state  $|n\rangle$  of the harmonic oscillator with energy  $\hbar\omega(n+1/2)$  a state with  $n$  quanta  $\hbar\omega$  of energy plus the zero point energy  $\hbar\omega/2$ . These quanta are called **phonons** for systems where massive particles have oscillatory degrees of freedom, the state  $|n\rangle$  is a  $n$ -phonon state.

$$|n\rangle \longleftrightarrow n\text{-phonon state}. \quad (4.52)$$

The ladder operator  $a^\dagger$  operates as

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \quad (4.53)$$

and creates a state with one more phonon which is why it is called a **creation operator**. In the same way, the operator  $a$ ,

$$a|n\rangle = \sqrt{n}|n-1\rangle \quad (4.54)$$

leads to a state with one phonon less (it destroys one phonon) and is called a **annihilation operator**.

In a similar manner, the oscillatory degrees of freedom of the electromagnetic field (light) lead to a Hamiltonian like the one of the harmonic oscillator. The corresponding states are called  $n$ -photon states. This is one of the topics of Quantum Mechanics II, the theory of light, and many-body theory. It is there where operators like the  $a$  and  $a^+$  show their full versatility and power.

## 4.4 The Hydrogen Atom

### 4.4.1 Spherical Symmetric Potentials in 3 Dimensions

The stationary Schrödinger equation in three dimensions

$$\left[ -\frac{\hbar^2 \Delta}{2m} + V(\mathbf{x}) \right] \Psi(\mathbf{x}) = E \Psi(\mathbf{x}) \quad (4.55)$$

contains the Laplace operator

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \quad (4.56)$$

For general  $V(\mathbf{x})$ , it is usually very difficult to solve this equation. There are, however, a few cases which are physically very important and can be solved exactly.

#### The Potential

We wish to determine the eigenfunctions  $\Psi(\mathbf{x})$  and possible energy eigenvalues  $E$  for a spherical symmetric potential

$$V(\mathbf{x}) = V(r), \quad r = |\mathbf{x}|. \quad (4.57)$$

An example for such a potential is the potential energy of the Coulomb attraction between a fixed point charge  $Ze > 0$  sitting at the origin  $\mathbf{x} = \mathbf{0}$  and a moving particle of mass  $m$  and charge  $-e$  at a distance  $r$  from the origin,

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}. \quad (4.58)$$

#### Polar Coordinates

It is useful to introduce **polar coordinates**

$$x = r \sin \theta \cos \varphi, \quad y = r \sin \theta \sin \varphi, \quad z = r \cos \theta \quad (4.59)$$

and to re-write the Laplacian in polar coordinates,

$$\Delta \Psi = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \Psi}{\partial \varphi^2} \right]. \quad (4.60)$$

The wave function  $\Psi = \Psi(r, \theta, \varphi)$  now depends on polar coordinates. We multiply the Schrödinger equation with  $r^2$ ,

$$\frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{2m}{\hbar^2} r^2 [E - V(r)] \Psi + \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \Psi}{\partial \varphi^2} \right] = 0,$$

which can be written with two operators  $\hat{h}$  and  $\hat{\Omega}$  as

$$\begin{aligned} \hat{h}\Psi + \hat{\Omega}\Psi &= 0 \\ \hat{h}\Psi &:= \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{2m}{\hbar^2} r^2 [E - V(r)] \Psi \\ \hat{\Omega}\Psi &:= \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \Psi}{\partial \varphi^2} \right]. \end{aligned}$$

The separation of  $r$ -dependences and angle dependences suggests a **separation Ansatz**, that is a wave function of the form

$$\Psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi). \quad (4.61)$$

Then,  $\hat{h}\Psi + \hat{\Omega}\Psi = 0$  means

$$\begin{aligned} \hat{h}R(r)Y(\theta, \varphi) + \hat{\Omega}R(r)Y(\theta, \varphi) &= Y(\theta, \varphi) \hat{h}R(r) + R(r) \hat{\Omega}Y(\theta, \varphi) = 0 \\ \rightsquigarrow \frac{1}{R(r)} \hat{h}R(r) &= -\frac{1}{Y(\theta, \varphi)} \hat{\Omega}Y(\theta, \varphi) =: -c. \end{aligned} \quad (4.62)$$

Here, we have used the fact that  $\hat{h}$  performs a differentiation with respect to  $r$  so that  $Y(\theta, \varphi)$  can be pulled in front of it. In the same way,  $\hat{\Omega}$  performs a differentiation with respect to  $\theta$  and  $\varphi$  only so that  $R(r)$  can be pulled in front of it. We thus have succeeded to completely separate the **radial part**  $R(r)$  from the **angular part**  $Y(\theta, \varphi)$ . The left side in (4.62) depends only on  $r$ , the right side only on  $\theta, \varphi$  whence both side must be a constant that we have denoted for convenience as  $-c$  here.

We first investigate the angular part as it can be solved exactly. The radial part can not be solved exactly for an arbitrary potential  $V(r)$ .

### 4.4.2 The Angular Part

The angular part of (4.62) in fact is again an eigenvalue problem, because the equation  $\hat{\Omega}Y = cY$  is an eigenvalue equation for the eigenvectors (eigenfunctions, remember that a function is a vector in a Hilbert space) and possible eigenvalues  $c$  of the operator  $\hat{\Omega}$ . Let us write down again this equation:

$$\left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \varphi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \varphi)}{\partial \varphi^2} \right] = cY(\theta, \varphi). \quad (4.63)$$

We do not explicitly construct the eigenfunctions  $Y$  of the operator  $\hat{\Omega}$  here but only give the results. In fact, this operator is closely related to the angular momentum operator which we will discuss in the next session. Similar to what we have found for the harmonic oscillator, it turns out that solutions of (4.63) are possible only for  $c = -l(l+1)$ , where  $l = 0, 1, 2, 3, \dots$  is an integer. All the solutions can be labeled by two quantum numbers  $l$  and  $m$ , where  $m$  is an integer that can take the values  $-l, -l+1, \dots, l-1, l$ . The solutions are called **spherical harmonics** and have the explicit form

$$\begin{aligned} Y_{lm}(\theta, \varphi) &= (-1)^{(m+|m|)/2} i^{|m|} \left[ \frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2} P_l^{|m|}(\cos \theta) e^{im\varphi} \\ P_l^{|m|}(x) &:= \frac{1}{2^l l!} (1-x^2)^{|m|/2} \frac{d^{l+|m|}}{dx^{l+|m|}} (x^2-1)^l \\ l &= 0, 1, 2, 3, \dots; \quad m = -l, -l+1, -l+2, \dots, l-1, l. \end{aligned} \quad (4.64)$$

The  $P_l^{|m|}$  are called **associated Legendre polynomials**. The spherical harmonics are an orthonormal function system on the surface of the unit sphere  $|\mathbf{x}| = 1$ . We write the orthonormality relation both in our abstract bra–ket and in explicit form:

$$\begin{aligned} |lm\rangle &\longleftrightarrow Y_{lm}(\theta, \varphi) & (4.65) \\ \langle l'm'|lm\rangle &= \delta_{ll'}\delta_{mm'} \longleftrightarrow \int_0^{2\pi} \int_0^\pi Y_{l'm'}^*(\theta, \varphi) Y_{lm}(\theta, \varphi) \sin\theta d\theta d\varphi = \delta_{ll'}\delta_{mm'}. \end{aligned}$$

The spherical harmonics with  $l = 0, 1, 2, 3, 4, \dots$  are denoted as  $s$ -,  $p$ -,  $d$ -,  $f$ -,  $g$ -,... functions which you might know already from chemistry ('orbitals'). The explicit forms for some of the first sphericals are

$$Y_{00} = \frac{1}{\sqrt{4\pi}}, \quad Y_{10} = i\sqrt{\frac{3}{4\pi}} \cos\theta, \quad Y_{1\pm 1} = \mp i\sqrt{\frac{3}{8\pi}} \sin\theta \cdot e^{\pm i\varphi}. \quad (4.66)$$

#### 4.4.3 The Radial Part

The radial part of the Schrödinger equation is obtained from (4.62) with  $c = -l(l+1)$ ,

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{2m}{\hbar^2} [E - V(r)] R(r) - \frac{l(l+1)}{r^2} R(r) = 0. \quad (4.67)$$

For the hydrogen atom, the attractive Coulomb potential generated by the proton (charge  $+e > 0$ ,  $Z = 1$ ) is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}. \quad (4.68)$$

Strictly speaking, we are now dealing with a problem where many particles are involved: the electron and the proton which itself is composed of smaller elementary particles, the quarks. In such cases our single particle Schrödinger equation is no longer strictly valid. We neglect the inner structure of the proton and also use the fact that it is much heavier than the electron. As in the case of other **two-body problems** one can introduce center-of-mass and relative coordinates and reduce the problem to a one-particle problem. The mass  $m$  is a reduced mass but it is very close to the electron mass.

Again, we do not explicitly solve for the possible energy eigenvalues  $E$  and the radial eigenfunctions here but present the result: For bound states where the electron is bound to the attractive potential, the possible eigenvalues  $E = E_n$  are labeled by a **quantum number**  $n$ ,

$$\begin{aligned} E_n &= -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} \frac{1}{n^2}, \quad n = 1, 2, 3, \dots \quad \text{Lyman Formula} \\ a_0 &:= \frac{4\pi\epsilon_0 \hbar^2}{me^2} \quad \text{Bohr Radius.} \end{aligned} \quad (4.69)$$

The radial eigenfunctions for the bound states are

$$\begin{aligned} R_{nl}(r) &= -\frac{2}{n^2} \sqrt{\frac{(n-l-1)!}{[(n+l)!]^3}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n+l}^{2l+1} \left(\frac{2r}{na_0}\right), \quad l = 0, 1, \dots, n-1 \quad (4.70) \\ L_n^m(x) &= (-1)^m \frac{n!}{(n-m)!} e^x x^{-m} \frac{d^{n-m}}{dx^{n-m}} e^{-x} x^n \quad \text{generalized Laguerre polynomials.} \end{aligned}$$

The wave functions of the bound states of the hydrogen atom (i.e. the attractive Coulomb potential (4.68)) are therefore given by the product of radial and angular part according to our separation ansatz (4.61),

$$\Psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_{lm}(\theta, \varphi). \quad (4.71)$$

## 4.5 The Angular Momentum

Symmetries play an important role in physics. The central potentials  $V(r)$  discussed above have *rotational symmetry*. From classical mechanics (Noether Theorem) we know that this implies the existence of a conserved quantity. In the case of rotational symmetry this means the conservation of angular momentum which is Kepler's second law.

### 4.5.1 Definitions

In classical mechanics, the angular momentum of an object with position  $\mathbf{x}$  and momentum  $\mathbf{p}$  is defined as

$$\mathbf{L} = \mathbf{x} \times \mathbf{p}, \quad (4.72)$$

that is the cross product (vector product) of the position and the momentum. In components, this is

$$\mathbf{L} = \begin{vmatrix} \cdot & \cdot & \cdot \\ x_1 & x_2 & x_3 \\ p_1 & p_2 & p_3 \end{vmatrix} = (x_2 p_3 - x_3 p_2, x_3 p_1 - x_1 p_3, x_1 p_2 - x_2 p_1). \quad (4.73)$$

The corresponding quantum mechanical operator is obtained from the correspondence principle that replaces  $\mathbf{x} \rightarrow \hat{\mathbf{x}}$ , i.e. the position operator, and  $\mathbf{p} \rightarrow -i\hbar\nabla$ , i.e. the momentum operator. Because we are in three dimensions, the operators are vectors:

$$\hat{\mathbf{x}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3), \quad \mathbf{p} = -i\hbar\nabla = -i\hbar(\partial_{x_1}, \partial_{x_2}, \partial_{x_3}) = (\hat{p}_1, \hat{p}_2, \hat{p}_3). \quad (4.74)$$

The angular momentum operator therefore becomes

$$\hat{\mathbf{L}} = -i\hbar\hat{\mathbf{x}} \times \nabla = (\hat{x}_2 \hat{p}_3 - \hat{x}_3 \hat{p}_2, \hat{x}_3 \hat{p}_1 - \hat{x}_1 \hat{p}_3, \hat{x}_1 \hat{p}_2 - \hat{x}_2 \hat{p}_1). \quad (4.75)$$

In polar coordinates, one has to use the spherical polar expression for the Nabla operator that you learned in vector analysis. The corresponding expression for the components of the angular momentum operator become

$$\begin{aligned} \hat{L}_x &= -i\hbar \left( -\sin\varphi \frac{\partial}{\partial\theta} - \cos\varphi \cot\theta \frac{\partial}{\partial\varphi} \right) \\ \hat{L}_y &= -i\hbar \left( \cos\varphi \frac{\partial}{\partial\theta} - \sin\varphi \cot\theta \frac{\partial}{\partial\varphi} \right) \\ \hat{L}_z &= -i\hbar \frac{\partial}{\partial\varphi}. \end{aligned} \quad (4.76)$$

Notice that in spherical polar coordinates, the  $z$ -axis is the central axis of the coordinate system with the angle  $\varphi$  revolving around it. The angular momentum  $L_z$  corresponds to revolutions around the  $z$ -axis, its quantum mechanical expression becomes quite simple: basically, just a differentiation with respect to the angle  $\varphi$  'around the  $z$  axis'.

Another important observation is that the **angular momentum square**, that is the operator  $\hat{\mathbf{L}}^2$ , becomes

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right]. \quad (4.77)$$

We notice that this is just  $-\hbar^2$  times the expression  $\hat{\Omega}$ , eq. (4.61), for the angular part of the Laplacian  $\Delta$ ! In particular, the eigenfunctions  $Y_{lm}$  of  $\hat{\Omega}$  are the eigenfunctions of the angular momentum square, cf. eq.(4.63) with  $c = -l(l+1)$ ,

$$\hat{\mathbf{L}}^2 Y_{lm}(\theta, \varphi) = \hbar^2 l(l+1) Y_{lm}(\theta, \varphi), \quad l = 0, 1, 2, 3, \dots \quad (4.78)$$

Furthermore, the dependence of  $Y_{lm}(\theta, \varphi)$  on the angle  $\varphi$  is only through the exponential  $e^{im\varphi}$ . We thus have

$$\hat{L}_z Y_{lm}(\theta, \varphi) = \hbar m Y_{lm}(\theta, \varphi), \quad (4.79)$$

which means that  $Y_{lm}(\theta, \varphi)$  are eigenfunctions of the  $z$ -component of the angular momentum, too.

The eigenfunctions  $\Psi_{nlm}(r, \theta, \varphi)$  of the Hamiltonian  $\hat{H}$  for the *hydrogen atom* therefore are also eigenfunctions of  $\hat{\mathbf{L}}^2$  and  $\hat{L}_z$ . We summarize this in three equations

$$\begin{aligned} \hat{H} \Psi_{nlm}(r, \theta, \varphi) &= E_n \Psi_{nlm}(r, \theta, \varphi) \\ \hat{\mathbf{L}}^2 \Psi_{nlm}(r, \theta, \varphi) &= \hbar^2 l(l+1) \Psi_{nlm}(r, \theta, \varphi) \\ \hat{L}_z \Psi_{nlm}(r, \theta, \varphi) &= \hbar m \Psi_{nlm}(r, \theta, \varphi). \end{aligned} \quad (4.80)$$