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1

Matter Waves

1.1 De Broglie's Matter Waves

In 1924 de Broglie postulated the existence of waves related with matter. He assumed that the momentum of a free particle is related to the wavelenght λ, or the wave number $k = \frac{2\pi}{\lambda}$ of the wave, according to

$$p = \frac{h}{\lambda} = \hbar k \tag{1.1}$$

The energy of a free particle in classical mechanics is given by

$$E = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}\frac{(\hbar k)^2}{2m} \tag{1.2}$$

Light	Matter
$E = h\nu$	$E = h\nu = \frac{(\hbar k)^2}{2m}$
$p = \frac{h\nu}{c}$	$p = \frac{h}{\lambda} = \hbar k$

Let us calculate the de'Broglie wavelength for some particles:

a) Electrons, accelerated by an electric field

$$\frac{p^2}{2m} = eU \qquad \lambda = \frac{h}{\sqrt{2eUm_e}} = \frac{1,226nm}{\sqrt{U/V}} \tag{1.3}$$

U=1000 V	$\lambda = 3.910^{-11}m$
U=100 V	$\lambda = 1.210^{-10}m$

b) Macroscopic particles:

$$m = 10^{-6}g, v = 10m/sec\lambda = 6.610^{-26}m \tag{1.4}$$

1921	Ramsauer	Scattering of slow electrons with gas atoms
1924	De Broglie	Postulation of the existence of matter waves
1926	E. Schrödinger	Formulation of the Schrödinger equation
1927	Davisson and Germer	Interference patterns in the intensity of electrons reflected from a crytsal surface
1927	W. Heisenberg	Formulation of the uncertainty relation
1931	Stern, Frisch, Estermann	Interference Experiments with Helium atoms
1956	Möllenstedt	Fresnel double slit experiment with electrons

1.2 Matter Waves: Experiments

1.2.1 Davisson-Germer Experiment

The Davisson-Germer Experiment directly verifies the hypotheses of de Broglie's concerning matter waves. It uses a beam of electrons, i.e. objects with a certain energy E and momentum p, in a typical diffraction experiment. The experimental arrangement is the one used for Bragg reflection using x-ray's. First, one investigates whether a kind of Bragg reflection pattern is observed. From the Bragg condition,

$$\lambda = 2dsin\theta \tag{1.5}$$

one determines the wavelength of the reflection pattern.

The outcomes of the experiments are:

- One detects the typical interference patterns of Bragg reflection.
- The Bragg condition for constructive interference allows one to determine the wave length λ.
- The measurement of the momentum of the electrons allows one to calculate the de Broglie's wave length λ.
- This wavelenght coincides with the one obtained form the hypothesis of de Broglie.

The Davisson-Germer experiment directly adresses the hypothesis of de Broglie. The electrons are accelerated in a electric field with voltage difference U. It gains the kinetic energy

$$E = \frac{p^2}{2m} = eU \tag{1.6}$$

This relationship allows one to calculate the momentum

$$p = \sqrt{2meU} \tag{1.7}$$

According to de Broglie's hypothesis, this should correspond to a wavelenth

$$\lambda = \frac{h}{p} \tag{1.8}$$

This wavelenght should be related to the scattering angle, in the same way as it would be for the case of x-ray-scattering. If we denote the lattice spacing by d constructive interference is obtained for the angles

$$\lambda = 2ndsin\theta \tag{1.9}$$

where n denotes the various interference maxima. As a consequence, there is a direct relationship between the angle θ and the kinetic energy of the electrons:

$$\sin\theta = \frac{1}{2nd}\frac{h}{p} = \frac{1}{2nd}\frac{h}{\sqrt{2emU}} \tag{1.10}$$

From x-ray scattering experiments using nickel crystals the lattice spacing of

$$d = 0.091nm \tag{1.11}$$

is obtained. The potential difference in the experiment was

$$U = 54V \tag{1.12}$$

This yields a de Broglie wavelength of

$$\lambda = 0.165nm \tag{1.13}$$

The first maximum then, should be, close to 50 degree. This is actually observed in the experiment: The Davisson-Germer experiment is a direct verification of the hypothesis of de Broglie.

C. Davisson, L. H. Germer; Reflections of a electrons by a crystal of Nickel, Nature 119, 558-560 (1927)

1.2.2 Diffraction Experiment of Möllenstedt and Düker

The Fresnel double prism experiment is a fundamental experiment in classical optics. The analog of the experiment carried out with electrons has been performed by Möllenstedt and Düker. The experimental arrangement is depicted in figure . The double prism has been realized for electrons by a quartz fibre located perpendicular to the electron beam. A voltage is induced between the fibre and the counterelectrodes, which depends on the current flowing through the voltage. The electrons are deflected by the inhomogenous electrical field.

1.2.3 Double Slit Experiment

C. Jönsson, Zeitschrift fr Physik 161, 454-474 (1961)

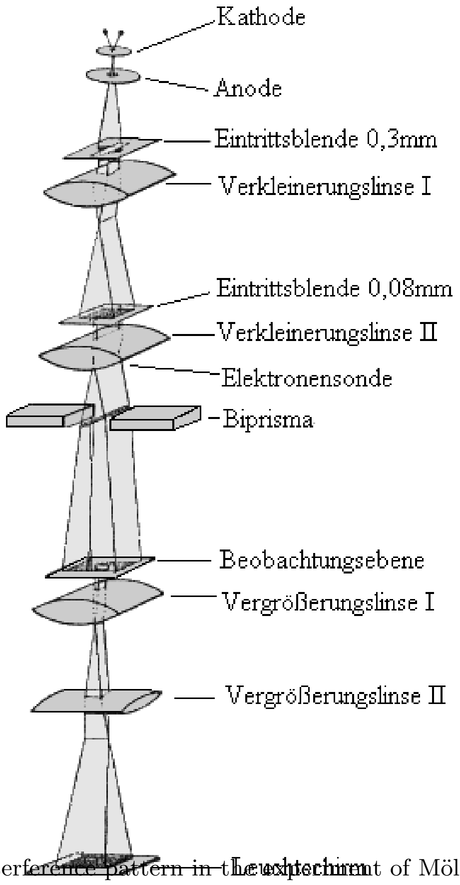
1.2.4 Tonomura

One can imagine that one lowers the intensity of the electron beam in a double slit experiment or another diffraction experiment so that, in fact, only a single electron passes the slits. This electron hits the screen at a certain point reflecting its pointlike behaviour. Such an experiment actually has been performed by Tonomura et al. Their results are exhibited in fig. (1.2.4). The first hits of electrons on the screen lead to a kind of random appearance of the hits. With increasing number of impinging electrons the well-known interference patterns emerge. This point to the fact the wave function contains information, which has to be interpreted in a statistical sense.

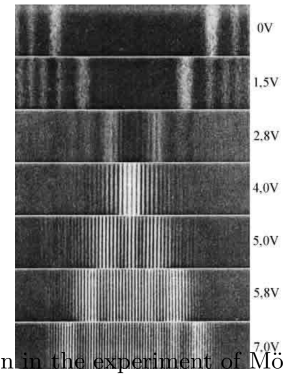
A. Tonomura, J. Enod, T. Matsuda, T. Kawasaki, and H. Exawa, Demonstration of single-elctron biuldup of an interference pattern,Amer. J. Phys. **57**, 117 (1989)

1.3 Interpretation of the Wave Function

De Broglie has assigned a wave function to each particle. This leads us to the problem of the *interpretation of the wave function* $\Psi(x,t)$.

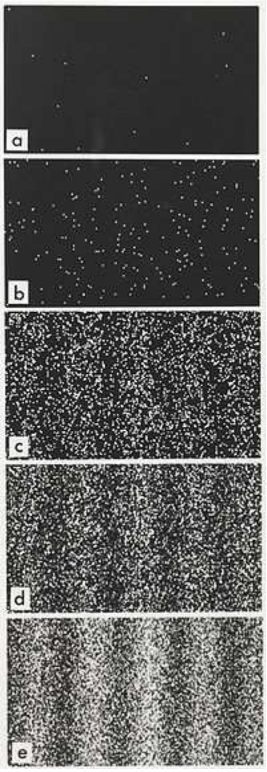


Interference pattern in the experiment of Möllenstedt and Düker.



Interference pattern in the experiment of Möllenstedt and Düker.

Interference pattern in the double slit experiment of Jönsson.



Emergence of interference pattern in the double slit experiment of Tanamura.

If we reconsider the double slit experiment of Tonomura, we recall that the interference patterns in the double slit experiment only develops gradually if a whole ensemble of electrons has passed the slits. For a single event, it is not possible to predict where the particle hits the counter. This introduces a probabilistic element: We relate the intensity of the wave, $|\psi(x,t)|^2$, to the emerging interference pattern. To this end we interpret

$$|\Psi(x,t)|^2 dx \tag{1.14}$$

as the probability to find the particle in the interval $[x, x+dx]$.

Based on this interpretation we can define the expectation of the position $\langle x(t) \rangle$ of the particles. This quantity is defined according to

$$\langle x(t) \rangle = \int x |\Psi(x,t)|^2 dx \tag{1.15}$$

Furthermore, we can determine higher order moments of the position,

$$\langle x(t)^n \rangle = \int x^n |\Psi(x,t)|^2 dx \tag{1.16}$$

1.4 Wave Packets

We shall now consider the wave function, which according to de'Broglie, is assigned to a free particle. To this end we start with a monochromatic wave, i.e. a wave characterized by a single frequency and wavelength, which can be represented by the complex function $\Psi(x,t)$

$$\Psi(x,t) = a e^{i(kx-\omega t)} \tag{1.17}$$

If we now take the expressions for matter waves due to de Broglie,

$$\begin{aligned} E &= \hbar\omega(k) = \frac{\hbar^2 k^2}{2m} \\ p &= \hbar k \qquad , \end{aligned} \tag{1.18}$$

we obtain

$$\Psi(x,t) = a e^{\frac{i}{\hbar}(px-Et)} = a e^{i(kx-\omega(k)t)} \tag{1.19}$$

However, such a wave is an infinitely extended object. In order to deal with localized particles one has to consider *wave packets*.

Wave packets are linear superpositions of monochromatic waves:

$$\Psi(x,t) = \int dk a(k) e^{i(kx-\omega(k)t)} \tag{1.20}$$

We consider the following example of a wave packet:

$$a(k) = \{ \begin{matrix} a & k_0 - \Delta k < k < k_0 + \Delta k \\ 0 & otherwise \end{matrix} \tag{1.21}$$

For sufficiently small values of Δk we can aproximate $\omega(k)$ by a Taylor series:

$$\omega(k) = \omega(k_0) + (k - k_0)\omega'(k_0) + ... \tag{1.22}$$

Based on this approximation we evaluate the integral and obtain

$$\begin{aligned} \Psi(x,t) &= ae^{i(k_0 x - \omega(k_0)t)} \int_{-\Delta k}^{\Delta k} dk' e^{i(k'(x-\omega'(k_0)t)} \\ &= ae^{i(k_0 x - \omega(k_0)t)} \frac{sin\Delta k(x - \omega'(k_0)t)}{(x - \omega'(k_0)t)} \end{aligned} \tag{1.23}$$

The wave is a product of a *carrier wave*

$$ae^{i(k_0 x - \omega(k_0)t)} \tag{1.24}$$

as well as the *enveloppe*

$$\frac{sin\Delta k(x - \omega'(k_0)t)}{(x - \omega'(k_0)t)} \tag{1.25}$$

The maximum of the envelope moves with the *group velocity*

$$x = Vt = \omega'(k_0)t \tag{1.26}$$

For matter waves we can explicitly use the relationship $\omega(k_0) = \frac{\hbar k_0^2}{2m}$ and conclude that the velocity V is just

$$V = \frac{\hbar k_0}{m} = \frac{p}{m} \tag{1.27}$$

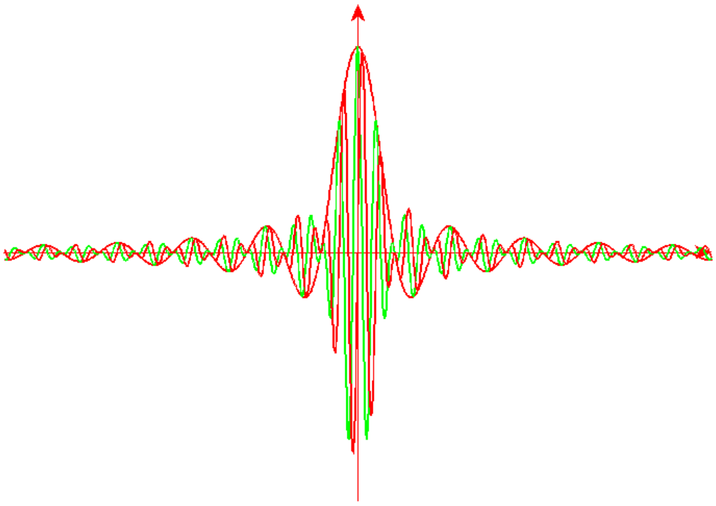
The width of the moving envelope can be defined as the distance between the two nearest zeros of the envelope, (1.25). It is given by $\Delta x \Delta k = 2\pi$ or, using the relationship $\Delta p = \hbar \Delta k$, by

$$\Delta x \Delta p = h \tag{1.28}$$

If we interpret Δx as the uncertainty of the location of the particle and Δp as the uncertainty to determine the momentum of the particle, we encounter through equation (**??**) an example of the *Heisenberg uncertainty relation.* This relationship demonstrates that it is not possible to sharply localize the particle $\Delta x \to 0$ and simultaneously have a sharply defined momentum $\Delta p \to 0$.

1.4.1 Gaussian Wave Packet

We investigate the Gaussian wave packet. This packet is defined by a Gaussian distribution of the amplitudes:



Wave packet

$$\Psi(x,t) = \int dk \frac{e^{-\frac{k^2}{2Q}}}{\sqrt{2\pi Q}} e^{i(kx-\hbar\frac{k^2}{2m}t} \tag{1.29}$$

We can easily evaluate this integral, since

$$\Psi(x,t) = \int dk e^{ikx} \frac{e^{-[\frac{1}{2Q}+i\frac{\hbar}{2m}t]}}{\sqrt{2\pi Q}} \tag{1.30}$$

is the Fourier-transform of a Gaussian integral, and as a consequence is also Gaussian.

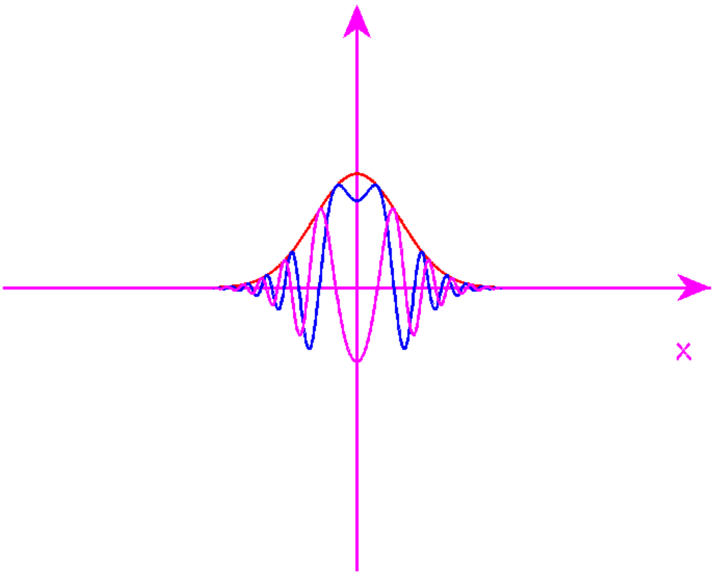
As can be seen from fig. an initially localized wave function spreads in the course of time.

1.4.2 Initial Condition

The amplitude $a(k)$ of a wave packet is determined by the wave packet at initial time $t = 0$:

$$\Psi(x,0) = \int dk a(k) e^{ikx} \tag{1.31}$$

This relation shows that the initial wave packet $\psi(x,0)$ and the amplitude $a(k)$ are related by Fourier transform. The inverse transform yields



Gaussian wave packet

$$a(k) = \frac{1}{2\pi} \int dx \psi(x, 0) e^{-ikx} \tag{1.32}$$

We explicitly see, that the wave function at time t is related to the function at time $t = 0$, since

$$\Psi(x, t) = \int dk \frac{1}{2\pi} \int dx' \Psi(x', 0) e^{ik[(x-x')-\omega(k)t]} \tag{1.33}$$

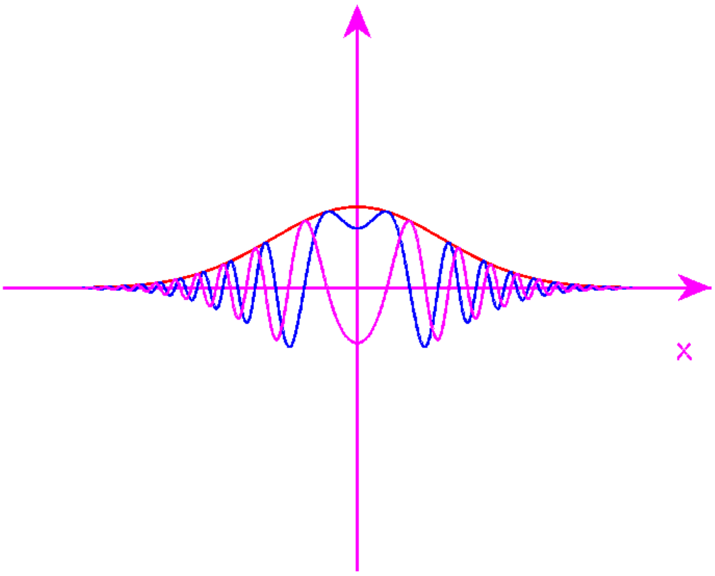
1.5 Particle in a Box

In this section, we shall treat the wave mechanics of a particle moving in a finite box. This means, that the regions $x < 0$ and $x > L$ are not allowed. Mathematically, we have to assume that the wave function of the particle has to become zero at $x = 0$ and $x = L$. This problem can be seen as a crude model of an electron moving in the potential of a nucleus.

We start from the de'Broglie's wave

$$\Psi(x, t) = a e^{i(kx-\omega(k)t)} \tag{1.34}$$

In order to take into account the barriers at $x = 0$, $x = L$ we make a superposition of a wave with positive momentum, $p = \hbar k$, and negative momentum,



Evolution of Gaussian wave packet.

$p = -\hbar k$,:

$$\Psi(x,t) = a_1 e^{i(kx-\omega(k)t)} + a_2 e^{i(-kx-\omega(-k)t)} \tag{1.35}$$

Since

$$\omega(-k) = \frac{\hbar(-k)^2}{2m} = \omega(k) \tag{1.36}$$

We can combine this superposition into

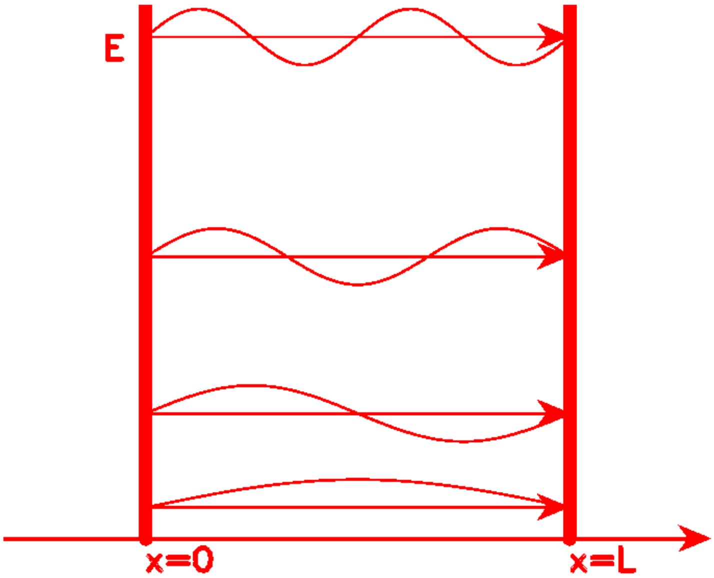
$$\Psi(x,t) = \left[csin(kx) + dcos(kx)\right] e^{-i\omega(k)t} \tag{1.37}$$

We have to fullfill the boundary conditions

$$\Psi(0,t) = 0 \qquad ; \qquad \Psi(L,t) = 0 \tag{1.38}$$

The first condition leads us to d=0. The second condition leads us to a restriction of momentum, i.e. the wave number k:

$$kL = \pi n \qquad n = 1, 2, ... \tag{1.39}$$



Energy Eigenstates and Wave Functions
for a Particle in a Potential Well.

Quantization of Energy, Momentum

We obtain the following family of wave functions

$$\Psi_n(x,t) = c_n sin\frac{\pi n}{L} x e^{-i\frac{\hbar\pi^2 n^2}{L^2}t} \tag{1.40}$$

Since the number n is allowed to take the values $n = 1, .., \infty$ there is an infinite number of such functions, each characterized by a disrete set of momenta, and energies:

$$\begin{aligned} p_n &= \hbar k_n = h\frac{n}{L} \\ E_n &= \frac{h^2 n^2}{2mL^2} \\ \Psi_N(x,t) &= c_N sin\frac{\pi n}{L} x e^{-i\frac{E_n}{\hbar}t} = \psi_N(x) e^{-i\frac{E_n}{\hbar}t} \\ \psi_N(x) &= \sqrt{\frac{2}{L}} sin\frac{\pi n}{L} x \end{aligned} \tag{1.41}$$

We have normalized the functions $\psi_N(x)$ in such a way that

$$\int_0^L dx\psi_N(x)^2 = \int_0^L dx\psi_N(x)^2 = \frac{2}{L}\int_0^L dx sin^2\frac{\pi n}{L} x \tag{1.42}$$

Summarizing, we see that the momentum $\hbar k$ as well as the energy $E = \frac{\hbar^2 k^2}{2m}$ is not allowed to take any value. Due to the boundaries, the energies and momenta of the wave functions (1.41 are restricted to an infinite set of disrete values: Energy and momentum of a particle in a box are *quantized*. The wave functions differ in the number of knots in the interval $0 < x < L$. There are $n - 1$ knots of the wave function $\psi_n(x)$.

The lowest energy value is

$$E_1 = \frac{h^2}{2m} \tag{1.43}$$

and the smallest absolute value of the momentum is

$$p_1 = \frac{h}{L} \tag{1.44}$$

Furthermore, we have the following relation

$$p_n L = nh \qquad n = 1, ..., \infty \tag{1.45}$$

Linear Superposition

We can generate other wave functions in terms of a *linear superposition* of the wave functions (1.41)

$$\Psi(x,t) = \sum_{n=1}^{\infty} C_n \psi_n(x) e^{-i\frac{E_n}{\hbar}t} \tag{1.46}$$

with arbitrary coefficients C_n. These coefficients, however, are determined from the initial condition $\Psi(x,0)$, since

$$\Psi(x,0) = \sum_{n=1}^{\infty} C_n \psi_n(x) = \sum_{n=1}^{\infty} C_n \sqrt{\frac{2}{L}} sin \frac{n\pi}{L} x \tag{1.47}$$

It is possible to invert this relationship by considering the following property of the functions $\psi_n(x)$:

$$\int_0^L dx \psi_n(x) \psi_M(x) = \delta_{nm} \tag{1.48}$$

Multiplying equation (**??**) by $\psi_m(x)$ and integrating over the interval $0 < x < L$, we obtain

$$\int_0^L dx \psi_m(x) \Psi(x,0) = \sum_{n=1}^{\infty} C_n \int_0^L dx \psi_m(x) \psi_n(x) = \sum_{n=1}^{\infty} C_n \delta_{nm} = C_m \tag{1.49}$$

The reader will have recognized that eq. (1.47) is a Fourier representation of $\Psi(x,0)$. Therefore, each initial wave function can be represented in the above manner.

Interpretation of Wave Function

We have seen that the function $\psi_n(x)$ belongs to the energy value $E_n = \frac{h^2}{2mL^2}$. The wave function is a linear superposition of these wave functions. We have already seen that the probability to find the particle in a small interval at location x is given by

$$p(x, dx) = |\Psi(x,t)|dx \tag{1.50}$$

In a similar way, we can assign a statistical interpretation to the amplitudes C_n. To this end we do not characterize the particle by its location, but by its energy. Energy of the particle is quantized and we can ask for the probability $p(E_n)$ to measure a particle with energy E_n. It is straightforward to postulate that the probability to measure the energy value E_n is given by

$$p(E_n) = |C_n|^2 \tag{1.51}$$

For example, the wave function

$$\Psi(x,t) = C_1\psi_1(x)e^{-i\frac{E_1}{\hbar}t} + C_2\psi_2(x)e^{-i\frac{E_2}{\hbar}t} \tag{1.52}$$

describes an experiment, in which, by measuring the energy, the energy E_1 would be obtained with probability $p(E_1) = |C_1|^2$ and the energy E_2 with probability $p(E_1) = |C_1|^2$.

2

Schrödinger Equation

The Schrödinger equation is an evolution equation for the wave function $\Psi(\mathbf{x}, t)$, which allows one to determine $\Psi(x, t)$ given an initial wave function $\Psi(x, 0)$. The Schrödinger equation was formulated by E. Schrödinger in 1926.

The Schrödinger equation replaces Newton's law for quantum particles.

2.1 Free particle

We consider the general form of De Broglie's matter waves for a free particle moving along a line.

$$\psi(x,t) = \int dk a(k) e^{i(kx - \frac{\hbar k^2}{2m} t)} \tag{2.1}$$

Just as electromagnetic waves are described by the wave equation, one may look for an equation, whose solution yields the matter waves.

One can calculate the temporal derivative of $\psi(x, t)$:

$$\frac{\partial}{\partial t}\Psi(x,t) = \int dk \left(-i\frac{\hbar k^2}{2m}\right) a(k) e^{i(kx - \frac{\hbar k^2}{2m} t)} \tag{2.2}$$

However, the right hand side can be expressed as a second derivative with respect to the coordiante x:

$$\frac{\partial^2}{\partial x^2}\Psi(x,t) = \int dk \left(-k^2\right) a(k) e^{i(kx - \frac{\hbar k^2}{2m} t)} \tag{2.3}$$

Combining eqs. (2.2) and (2.3) we obtain the evolution equation for the de Broglie matter wave:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) \tag{2.4}$$

This equation has been formulated by E. Schrödinger and is denoted as the Schrödinger equation for a free particle moving along a line.

2.2 Free Particle in Three Dimensions

We generalize our treatment to the case of a free particle in three dimensions. To this end we have to take into account that the momentum of a particle is a vectorial quantity

$$\begin{aligned} E &= \frac{\mathbf{p}^2}{2m} = \frac{\hbar^2 \mathbf{k}^2}{2m} = \hbar\omega(k) \\ \mathbf{p} &= \hbar\mathbf{k} \end{aligned} \tag{2.5}$$

A matter wave, therefore, has the form

$$\psi(\mathbf{x}, t) = \int d^3\mathbf{k} a(\mathbf{k}) e^{i(\mathbf{k}\cdot\mathbf{x} - \omega(k)t)} \tag{2.6}$$

We can formulate the following evolution equation for the wave function of a free particle in the infinite, three-dimensional space

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{x}, t) = -\frac{\hbar^2}{2m} \Delta\psi(\mathbf{x}, t) \tag{2.7}$$

2.3 Particle in a Potential

We generalize our treatment to the motion of a particle in an external potential $U(\mathbf{x})$. The total energy for a particle in an external potential $U(\mathbf{x})$ is just

$$E = H(p, x) = \frac{\mathbf{p}^2}{2m} + U(\mathbf{x}) \tag{2.8}$$

As a consequence, we extend the Schrödinger equation as follows:

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{x}, t) = -\frac{\hbar^2}{2m} \Delta\psi(\mathbf{x}, t) + U(\mathbf{x})\psi(\mathbf{x}, t) \tag{2.9}$$

2.3.1 Linear Superposition

The Schrödinger equation is a linear equation. Linearity implies the validity of the superposition principle: Provided $\Psi_I(\mathbf{x}, t)$ and $\Psi_{II}(\mathbf{x}, t)$ are solutions then the superposed solution is a solution of the Schrödinger equation

$$\Psi(\mathbf{x}, t) = N \left[\Psi_I(\mathbf{x}, t) + \Psi_{II}(\mathbf{x}, t)\right] \tag{2.10}$$

However, the interpretation of the wave function $|\Psi(x, t)|^2$ as a probability density requires the proper normalization of the sum.

2.4 Wave Function: Statistical Interpretation

As we have already emphasized the wave function has a statistical interpretation. The quantity

$$\rho(x,t)dx = |\psi(x,t)|^2 dx = \psi(x,t)^* \psi(x,t) dx \tag{2.11}$$

denotes the probability to find a particle in the interval $[x, dx]$. To this end, the wave function has to be normalized:

$$\int |\psi(x,t)|^2 dx = \int \psi(x,t)^* \psi(x,t) dx = 1 \tag{2.12}$$

2.4.1 Probability Density, Current: 1 D

Particle in 1D

Since the probability has to be conserved,

$$\int_{-\infty}^{\infty} dx \rho(x,t) = 1 \tag{2.13}$$

the temporal evolution of the probability density has to obey a continuity equation

$$\frac{\partial}{\partial t}\rho(x,t) + \frac{\partial}{\partial x} j(x,t) = 0 \tag{2.14}$$

This equation implies that the normalization is conserved with respect to time

$$\frac{\partial}{\partial t}\int_{-\infty}^{\infty} dx \rho(x,t) = -\int_{-\infty}^{\infty} dx \frac{\partial}{\partial x} j(x,t) = -[j(\infty,t) - j(-\infty,t)] = 0 \tag{2.15}$$

We have to proof that the existence of the continuity equation is compatible with the Schrödinger equation. To this end we determine the temporal evolution of the probability density $\rho(x,t)$

$$\frac{\partial}{\partial t}\rho(x,t) = \Psi(x,t)^* \frac{\partial}{\partial t}\Psi(x,t) + \Psi(x,t)\frac{\partial}{\partial t}\Psi(x,t)^* \tag{2.16}$$

from the Schrödinger equation:

$$\begin{aligned}
\Psi(x,t)^* \frac{\partial}{\partial t}\Psi(x,t) &= \frac{1}{i\hbar}\Psi(x,t)^* \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + U(x)\Psi(x,t) \right] \\
\Psi(x,t)\frac{\partial}{\partial t}\Psi(x,t)^* &= -\frac{1}{i\hbar}\Psi(x,t) \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)^* + U(x)\Psi(x,t)^* \right]
\end{aligned} \tag{2.17}$$

A straightforward calculation yields

$$\frac{\partial}{\partial t}\rho(x,t) = -\frac{\hbar}{2mi}\left[\Psi(x,t)^* \frac{\partial^2}{\partial x^2}\Psi(x,t) - \Psi(x,t)\frac{\partial^2}{\partial x^2}\Psi(x,t)^* \right] \tag{2.18}$$

which can easily be transformed into

$$\frac{\hbar}{2mi}\frac{\partial}{\partial x}\left[\Psi(x,t)^*\frac{\partial}{\partial x}\Psi(x,t)-\Psi(x,t)\frac{\partial}{\partial x}\Psi(x,t)^*\right] \tag{2.19}$$

Let us summarize: We have shown that the probability density $\rho(x,t)$ obeys a continuity equation (2.14) with the probability density $\rho(x,t)$ and the probability current $j(x,t)$

$$\begin{aligned}\rho(x,t) &= |\psi(x,t)|^2 \\ j(x,t) &= \frac{\hbar^2}{2mi}[\psi(x,t)^*\frac{\partial}{\partial x}\psi(x,t)-\psi(x,t)\frac{\partial}{\partial x}\psi(x,t)^*]\end{aligned} \tag{2.20}$$

The continuity equation directly follows from the Schrödinger equation. This underlines the fact that the probabilistic interpretation and the temporal evolution of the wave function are compatibel.

2.4.2 Probability Density, Current: 3D

We perform the determination of probability current and density for a particle in 3 dimensional space. The density and current are related by the continuity equation

$$\frac{\partial}{\partial t}\rho(\mathbf{x},t)+\nabla\cdot\mathbf{j}(\mathbf{x},t)=0 \tag{2.21}$$

The Schrödinger equation yields

$$\begin{aligned}\frac{\partial}{\partial t}\Psi(\mathbf{x},t)^*\Psi(\mathbf{x},t) &= \Psi(\mathbf{x},t)^*\frac{\partial}{\partial t}+\Psi(\mathbf{x},t)\frac{\partial}{\partial t}^{*} \\ &\frac{1}{i\hbar}\ \{\ \Psi(\mathbf{x},t)^*\frac{-\hbar^2}{2m}\Delta\Psi(\mathbf{x},t)-\Psi(\mathbf{x},t)\frac{-\hbar^2}{2m}\Delta\Psi(\mathbf{x},t)^*\}\end{aligned} \tag{2.22}$$

Furthermore, we make use of the identity

$$\nabla\cdot[\Psi(\mathbf{x},t)^*\nabla\Psi(\mathbf{x},t)]=\nabla\cdot\Psi(\mathbf{x},t)^*\cdot\nabla\Psi(\mathbf{x},t)]+[\Psi(\mathbf{x},t)^*\Delta\Psi(\mathbf{x},t)] \tag{2.23}$$

and are led to the continuity equation

$$\frac{\partial}{\partial t}\rho(\mathbf{x},t)+\nabla\cdot\frac{\hbar}{2mi}[\Psi(\mathbf{x},t)^*\nabla\Psi(\mathbf{x},t)-\Psi(\mathbf{x},t)\nabla\Psi(\mathbf{x},t)^*]=0 \tag{2.24}$$

The probability current is given by

$$\mathbf{j}=\frac{\hbar}{2mi}\{\Psi(\mathbf{x},t)^*\nabla\Psi(\mathbf{x},t)-\Psi(\mathbf{x},t)\nabla\Psi(\mathbf{x},t)^*\} \tag{2.25}$$

2.5 Expectations, Operators, Brackets

2.5.1 Expectation of Momentum

The expectation value $\langle \mathbf{x}(t) \rangle$ of the position of a particle is determined by the average

$$\langle \mathbf{x}(t) \rangle = \int d\mathbf{x} \mathbf{x} \rho(\mathbf{x}, t) \tag{2.26}$$

The question arises, how one can define the expectation of momentum.

In classical mechancis, momentum is defined via the relation

$$m\dot{\mathbf{x}} = \mathbf{p} \tag{2.27}$$

In quantum mechanics, we can only talk expectation, due to the probabilistic nature of single experiments. Therefore, we define the expectation of momentum by the relation

$$m\langle \dot{\mathbf{x}} \rangle = \langle \mathbf{p} \rangle \tag{2.28}$$

It is straightforward to determine the temporal derivative of

$$\begin{aligned} \frac{d}{dt}\langle \mathbf{x}(t) \rangle &= \int d\mathbf{x} \mathbf{x} \frac{\partial}{\partial t} \rho(\mathbf{x}, t) \\ &= -\int d\mathbf{x} \mathbf{x} \nabla \cdot \mathbf{j}(\mathbf{x}, t) \end{aligned} \tag{2.29}$$

Thereby, we have made use of the continuity equation for the probability density $\rho(\mathbf{x}, t)$. Partial integration yields

$$\frac{d}{dt}\langle \mathbf{x}(t) \rangle = \int d\mathbf{x} \mathbf{j}(\mathbf{x}, t) \tag{2.30}$$

Now, we can use the representation of the probability current

$$\frac{d}{dt}\langle \mathbf{x}(t) \rangle = \frac{\hbar}{2mi} \int d\mathbf{x} [\Psi(\mathbf{x}, t)^* \nabla \Psi(\mathbf{x}, t) - \Psi(\mathbf{x}, t) \nabla \Psi(\mathbf{x}, t)^*] \tag{2.31}$$

A second partial integration yields

$$\langle p(t) \rangle = m \frac{d}{dt} \langle \mathbf{x}(t) \rangle = \int d\mathbf{x} \Psi(\mathbf{x}, t)^* \frac{\hbar}{i} \nabla \Psi(\mathbf{x}, t) \tag{2.32}$$

2.5.2 Momentum Operator

We can compare the expectation values of position and momentum:

$$\langle \mathbf{x}(t) \rangle = \int d\mathbf{x} \Psi(\mathbf{x}, t)^* \mathbf{x} \Psi(\mathbf{x}, t) \tag{2.33}$$

$$\langle \mathbf{p}(t) \rangle = \int d\mathbf{x} \mathit{\Psi}(\mathbf{x}, t)^* \frac{\hbar}{i} \nabla \mathit{\Psi}(\mathbf{x}, t) \tag{2.34}$$

This comparision suggests to introduce the momentum operator

$$\tilde{\mathbf{p}} = \frac{\hbar}{i} \nabla \tag{2.35}$$

to rewrite the expectation in terms of this momentum operator:

$$\langle \mathbf{p}(t) \rangle = \int d\mathbf{x} \mathit{\Psi}(\mathbf{x}, t)^* \tilde{\mathbf{p}} \mathit{\Psi}(\mathbf{x}, t) \tag{2.36}$$

2.5.3 Operators

We can view the operation $\tilde{\mathbf{p}}$ as a prescription to form the vector $\frac{\hbar}{i} \nabla \mathit{\Psi}(\mathbf{x}, t)$ from a wave function $\mathit{\Psi}(\mathbf{x}, t)$. In this sense, we can also introduce the operator $\tilde{\mathbf{x}}$, which generates the vector $\mathbf{x} \mathit{\Psi}(\mathbf{x}, t)$ from the wave function $\mathit{\Psi}(\mathbf{x}, t)$.

We can use the momentum operator in order to define further operators like

$$(\tilde{p}_x)^2 = (\frac{\hbar}{i} \frac{\partial}{\partial x}) = -\hbar^2 \frac{\partial^2}{\partial x^2} \tag{2.37}$$

or the operator

$$\begin{aligned} (\tilde{\mathbf{p}})^2 &= (\tilde{p}_x)^2 + (\tilde{p}_y)^2 + (\tilde{p}_z)^2 \\ &= = -\hbar^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\hbar^2 \mathit{\Delta} \end{aligned} \tag{2.38}$$

Furthermore, we can define operators which are composed of the position $\tilde{\mathbf{x}}$ and momentum $\tilde{\mathbf{p}}$.

2.5.4 Hamilton Operator

An further example of an operator is the so-called Hamilton operator, defined as

$$\tilde{H} = \frac{(\tilde{p})^2}{2m} + U(\tilde{\mathbf{x}}) \tag{2.39}$$

Using the representation of the momentum operator it is straightforward to formulate the Schrödinger equation in terms of the Hamilton operator

$$i\hbar \frac{\partial}{\partial t} \mathit{\Psi}(\mathbf{x}, t) = \tilde{H} \mathit{\Psi}(\mathbf{x}, t) \tag{2.40}$$

2.5.5 Brackets

It is convenient to introduce a shorthand notation for the integrals occuring in the expressions for the expectations of position and momentum. We define

$$\langle \mathbf{x}(t) \rangle = \langle \mathit{\Psi}(\mathbf{x}, t) | \mathbf{x} | \mathit{\Psi}(\mathbf{x}, t) \rangle \tag{2.41}$$

as well as

$$\langle \mathbf{p}(t) \rangle = \langle \mathit{\Psi}(\mathbf{x}, t) | \mathbf{p} | \mathit{\Psi}(\mathbf{x}, t) \rangle \tag{2.42}$$

2.5.6 Expectations of Operators

In a similar way, we can define expectations for arbitrary operators $\tilde{O}$:

$$\langle \tilde{O} \rangle = \langle \Psi(\mathbf{x}, t) | \tilde{O} | \Psi(\mathbf{x}, t) \rangle \tag{2.43}$$

2.6 Quantization of Classical Mechanics

2.6.1 Classical Mechanics: Hamilton Formulation

The dynamics of a particle in classical mechanics can be described in terms of Hamilton's formulation. The Hamilton function is given in terms of the (generalized) positions $\mathbf{q}$ and momenta $\mathbf{p}$:

$$H = \frac{\mathbf{p}^2}{2m} + U(\mathbf{q}) \tag{2.44}$$

The equation of motion are given by Hamilton's equation

$$\dot{q}_i = \frac{\partial}{\partial p_i} H \qquad , \qquad \dot{p}_i = -\frac{\partial}{\partial q_i} H \tag{2.45}$$

Integration of these equations determines the position and momenta $\mathbf{q}(t), \mathbf{p}(t)$ from the initial conditions $\mathbf{q}(0), \mathbf{p}(0)$.

2.6.2 Quantization, Jordan Rules

We can perform the quantization of the classical theory due to the following steps:

- Introduction of a *wave function* $\Psi(\mathbf{x}, t)$
- Introduction of the *position and momentum operators* $\tilde{\mathbf{x}}$, $\tilde{\mathbf{p}}$.

$$\begin{aligned} \mathbf{q} &\rightarrow \tilde{\mathbf{x}} \\ \mathbf{p} &\rightarrow \tilde{\mathbf{p}} = \frac{\hbar}{i} \nabla \end{aligned} \tag{2.46}$$

- Introduction of the *Hamilton operator*:
  The replacement of position and momentum by the correponding operators in the classical Hamilton function $H(\mathbf{p}, \mathbf{q})$ leads to the Hamilton operator $\tilde{H}$

$$\tilde{H} = \frac{\tilde{\mathbf{p}}^2}{2m} + U(\tilde{\mathbf{x}}) \tag{2.47}$$

- The temporal evolution of the wave function $\Psi(\mathbf{x},t)$ is given by the Schrödinger equation
$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x},t) = \tilde{H}\Psi(\mathbf{x},t) \tag{2.48}$$
This equation allows one to determine the wave function $\Psi(\mathbf{x},t)$ from the initial condition $\Psi(\mathbf{x},0)$. It replaces Hamilton's equations (7.92) of classical mechanics.
- *Interpretation* of the wave function.
Expectations of location and momenta are given by
$$\begin{aligned}\langle\mathbf{x}(t)\rangle &= <\Psi(\mathbf{x},t)|\tilde{\mathbf{x}}|\Psi(\mathbf{x},t)\rangle\\ \langle\mathbf{p}(t)\rangle &= <\Psi(\mathbf{x},t)|\tilde{\mathbf{p}}|\Psi(\mathbf{x},t)\rangle\end{aligned} \tag{2.49}$$
- *Jordan's rules*:
a) An operator $\tilde{O}$ is assigned to each observable given by the classical expression $O(\mathbf{q},\mathbf{p})$. The outcome of the measurement of this observable is given by the expectation value
$$\langle\tilde{O}\rangle = \langle\Psi(\mathbf{x},t)|\tilde{O}|\Psi(\mathbf{x},t)> \tag{2.50}$$
b) The explicit expression of the operator $\tilde{O}$ is obtained by replacing $\mathbf{q}$ and $\mathbf{p}$ with the operators $\tilde{\mathbf{x}}$, $\tilde{\mathbf{p}}$:
$$\tilde{O} = O(\tilde{\mathbf{x}},\tilde{\mathbf{p}}) \tag{2.51}$$

Classical Quantity	Quantum Mechanical Operator
$\mathbf{q}$	$\mathbf{x}$
$\mathbf{p}$	$\frac{\hbar}{i}\nabla$
$U(\mathbf{q}$	$U(\mathbf{x})$
$T(\mathbf{p}) = \frac{\mathbf{p}^2}{2m}$	$-\frac{\hbar^2}{2m}\Delta$
$H(\mathbf{p},\mathbf{q})$	$\tilde{H} = -\frac{\hbar^2}{2m}\Delta + U(\mathbf{x})$
$\mathbf{L} = [\mathbf{q}\times\mathbf{p}]$	$\tilde{L} = \frac{\hbar}{i}[\mathbf{x}\times\nabla]$

3

Wave Mechanics in One Dimension

In this section we consider solutions of the Schrödinger equation in one dimension:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + U(x)\Psi(x,t) \tag{3.1}$$

3.1 Time Independent Schrödinger Equation

A first step in the treatment of the Schrödinger equation for a stationary potential is the separation ansatz:

$$\Psi(x,t) = e^{-i\frac{E}{\hbar}t}\psi(x) \tag{3.2}$$

This ansatz immediately leads us to the sc-called *time independent Schrödinger equation*

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + U(x)\psi(x) \tag{3.3}$$

This is a second order differential equation with respect to x, which has to be solved under the consideration of certain boundary conditions.

3.2 Free Particle on a Ring

The time independent Schrödinger equation for a free particle reads

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) \tag{3.4}$$

Thereby, we consider a particle on a ring-like configuration, i.e. we assume that the wave function $\Psi(x,t)$ and, consequently, $\psi(x)$ obey *periodic boundary conditions*

$$\psi(x) = \psi(x+L) \tag{3.5}$$

We can perform the following ansatz for the solution

$$\psi(x) = Ne^{ikx} \tag{3.6}$$

The periodic boundary condition requires a quantization of the wavenumber k:

$$k = \frac{2\pi}{L}n \qquad n = -\infty, ..., 0, ...\infty \tag{3.7}$$

The normalization constant is determined by the conditon

$$\int_0^L dx \psi(x)^* \psi(x) = N^2 L \tag{3.8}$$

Furthermore, we have the relation

$$\int_0^L dx \psi_k(x)^* \psi_l(x) = \delta_{kl} \tag{3.9}$$

Our ansatz solves the time independent Schrödinger equation provided the energy E is related to the wave number by

$$E_k = \frac{(\hbar k)^2}{2m} = (\frac{h}{L})^2 \frac{1}{2m} n^2 \tag{3.10}$$

We recover explicitly de Broglie's ansatz, $p = \hbar k$, for matter waves. However, due to periodic boundary conditions, the energy is quantized.

Since the Schrödinger equation is linear, a general solution is given by a linear superposition

$$\Psi(x,t) = \sum_k c_k \psi_k(x) e^{-i\frac{E(k)}{\hbar}t} \tag{3.11}$$

Thereby, the sum is over all k-values $k = 0, \pm\frac{2\pi}{L}, ...$

The coefficients are given by the initial condition:

$$\Psi(x,0) = \sum_k c_k \psi_k(x) \tag{3.12}$$

and, due to relation (3.16), we are able to determine the coefficients c_k according to

$$c_k = \int_0^L dx \psi_k(x) \Psi(x,0) = \int_9^L dx \frac{1}{\sqrt{L}} e^{-ikx} \Psi(x,0) \tag{3.13}$$

Inserting this representation of the coefficients c_k into (3.12) we obtain

$$\Psi(x,0) = \sum_k \psi_k(x) \int_0^L dx' \psi_k(x')^* \Psi(x',0) \tag{3.14}$$

This identity shows that the class of functions $\psi_k(x)$ obeys the so-called *completeness relation*

$$\sum_k \psi_k(x)\psi_k(x')^* = \delta(x-x') \tag{3.15}$$

Since the class of functions obeys the *orthogonality relation*

$$\int_0^L dx\psi_l(x)^*\psi_k(x) = \delta_{kl} \tag{3.16}$$

the set of functions form an *orthonormal basis*: Each periodic function can be expanded into a Fourier-series.

Let us reconsider our results. The wave function is given as a linear superposition of the functions $\psi_k(x)$:

$$\Psi(x,t) = \sum_k c_k\psi_k(x)e^{-i\frac{E_k}{\hbar}t} \tag{3.17}$$

They are obtained as a solution of the *boundary value problem*

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_k(x) &= E_k\psi_k(x) \\ \psi_k(0) = \psi_k(L) &= 0 \end{aligned} \tag{3.18}$$

This boundary value problem simultaneously determines the discrete set of energy values E_k, the so-called *energy spectrum*, as well as a complete orthonormal set of so-called *eigenfunctions*. The coefficients c_k can be determined from the initial condition using the orthonormality condition (3.16). Since the set of eigenfunctions is complete, each wave function obeying the periodic boundary conditions can be represented as a superposition: The eigenfunctions $\psi_k(x)$ form a *complete orthonormal set* of functions.

Let us now adress the question of the interpretation of the wave function $\Psi(x,t)$. We already now that the quantity $|\Psi(x,t)|^2 dx$ can be interpreted as a probability. However, the representation allows one to make a different interpretation. If we consider a wave function of the form

$$\Psi(x,t) = \psi_k(x)e^{-i\frac{E_k}{\hbar}t}c_k(0) \tag{3.19}$$

a single energy value E_k is involved, and, therefore, the corresponding particle has a definite energy value E_k.

3.2.1 Expectation of Position

The expectation value of the particle position is denoted as

$$\langle x(t)\rangle = \int_0^L dx\rho(x,t)x = \int_0^L dx\Psi(x,t)^* x\Psi(x,t) \tag{3.20}$$

3.2.2 Expectation of Momentum

We now want to determine the expectation value of momentum. We define this quantity according to the classical relation

$$\langle p(t)\rangle = m\frac{d}{dt}\langle x(t)\rangle = \int_0^L dx \varPsi^*(x,t)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\varPsi(x,t) \tag{3.21}$$

It is instructive to calculate this expectation using the representation of our wave function:

$$\begin{aligned}\langle p(t)\rangle &= \sum_k\sum_{k'}\int_0^L dx e^{i\frac{E_k-E_{k'}}{\hbar}t} c_k^* c_{k'} \psi_k^*(x)\frac{\hbar}{i}\frac{\partial}{\partial x}\psi_{k'}(x)\\ &= \sum_k \hbar k|c_k|^2\end{aligned} \tag{3.22}$$

However, this formula points out the physical interpretation of the coefficients c_k.

3.2.3 Hamilton Operator

The introduction of the momentum operator allows us to introduce the Hamilton operator

$$H = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \tag{3.23}$$

It is interesting to calculate the expectation of the energy in a similar way. We calculate

$$\langle\tilde{H}\rangle = \langle\varPsi(x,t)|\tilde{H}|\varPsi(x,t)\rangle = \int_0^L dx\varPsi(x,t)^*\tilde{H}\varPsi(x,t) \tag{3.24}$$

A similar calculation as in the previous section yields

$$\langle\tilde{H}\rangle = \sum |c_k|^2\frac{(\hbar k)^2}{2m} \tag{3.25}$$

This representation immediately yields the following interpretation of $|c_k|^2$: The quantity $|c_k|^2$ has to be interpreted as the probability to find a particle with the energy E_k.

3.3 Free Particle on the Line

Let us now consider the limit of infinite length $L \to \infty$. In this case the allowed k-values tend to the continuum and it is straightforward to replace the discrete sum by an integral. To this end we introduce the representation

$$\begin{aligned}\Psi(x,t) &= \sum_k \frac{1}{\sqrt{L}} c_k e^{ikx} e^{-i\hbar k^2/2mt} \\ &= \sum_k \Delta k C(k) \frac{1}{\sqrt{2\pi}} e^{ikx} e^{-i\hbar k^2/2mt} \\ &\to \int dk C(k) \frac{1}{\sqrt{2\pi}} e^{ikx} e^{-i\hbar k^2/2mt}\end{aligned} \tag{3.26}$$

where we have defined

$$\Delta k = \frac{2\pi}{L} \qquad c_k = \frac{C(k)}{\sqrt{2\pi L}} \tag{3.27}$$

The limit $L \to \infty$ means that we are going from a Fourier-series to a Fourier integral.

The coefficients $C(k)$ are then given by the inverse Fourier transform

$$\Psi(x,0) = \int dk C(k) \frac{1}{\sqrt{2\pi}} e^{ikx} \tag{3.28}$$

or,

$$C(k) = \int dx \Psi(x,0) \frac{1}{\sqrt{2\pi}} e^{-ikx} \tag{3.29}$$

Inserting this relationship back into (3.28) we arrive at the *completeness* relation

$$\int dk \frac{1}{2\pi} e^{ik(x-x')} = \delta(x-x') \tag{3.30}$$

which is a well-known representation of the δ-function.

3.4 Infinitely Deep Potential Well

Although we have already discussed the wave mechanics of a particle in an infinitely deep potential well, we shall reconsider this problem based on the solution of the Schrödinger equation.

To this end we consider the time independent Schrödinger equation

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) \tag{3.31}$$

together with the boundary conditions

$$\psi(x=0) = \psi(x=L) = 0 \tag{3.32}$$

These boundary conditions imply that the probability to find a particle close to the boundary vanishes.

The time independent Schrödinger equation is solved by the ansatz

$$\psi(x) = asinkx + bcoskx \tag{3.33}$$

provided we choose the energy

$$E = \frac{(\hbar k)^2}{2m} \tag{3.34}$$

The boundary condition $\psi(0) = 0$ leads us to $b = 0$, whereas the condition $\psi(L) = 0$ requires the quantization of the values of k

$$kL = \pi n \qquad n = 1, 2, ..., \infty \tag{3.35}$$

and, accordingly, a quantization of energy

$$E_n = \frac{(\hbar\pi)^2}{2mL^2} n^2 \tag{3.36}$$

Mathematical remarks:
The functions

$$\varphi_n(x) = \sqrt{\frac{2}{L}} sinn\frac{\pi}{L}x \tag{3.37}$$

form a complete function set. This means that each function with the boundary conditions

$$v(x = 0) = v(x = L) = 0 \tag{3.38}$$

can be expanded in a series according to

$$f(x) = \sum_n c_n \sqrt{\frac{2}{L}} sinn\frac{\pi}{L}x \tag{3.39}$$

Furthermore, we have the orthogonality relation

$$\int_0^L dx \sqrt{\frac{2}{L}} sinn\frac{\pi}{L}x \sqrt{\frac{2}{L}} sinm\frac{\pi}{L}x = \delta_{nm} \tag{3.40}$$

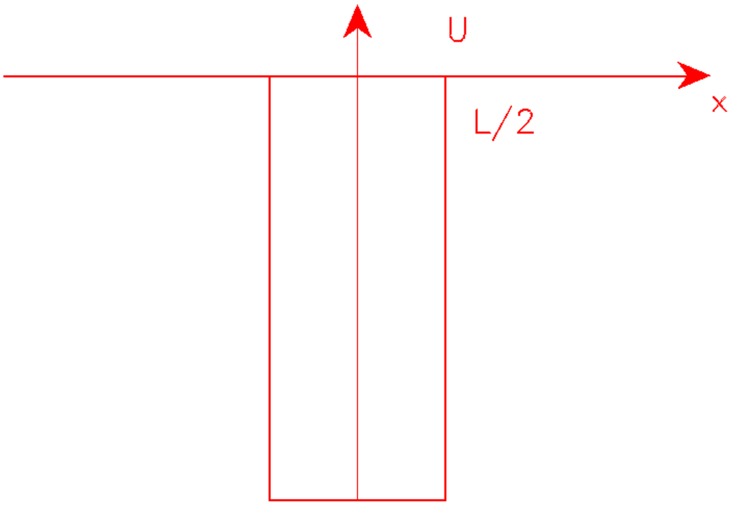
The function system is complete.

3.5 Particle in a Finite Potential Well

We consider the motion of a particle in the potential well exhibited in fig. (**??**)

$$U(x) = \{ \begin{matrix} -U_0 & |x| < L/2 \\ 0 & |x| > L/2 \end{matrix} \tag{3.41}$$

Classically, there are bounded states, if the energy of the particle is less then zero. In the case of positive energy, the particle can move freely. The behaviour of a quantum particle is similar, but we expect that the energy values are quantized in the bounded case.



Finite potential well.

3.5.1 Bounded States

We restrict the energy of the particle to

$$-U_0 < E < 0 \tag{3.42}$$

We have to solve the time independent Schrödinger equation

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + U(x)\psi(x) \tag{3.43}$$

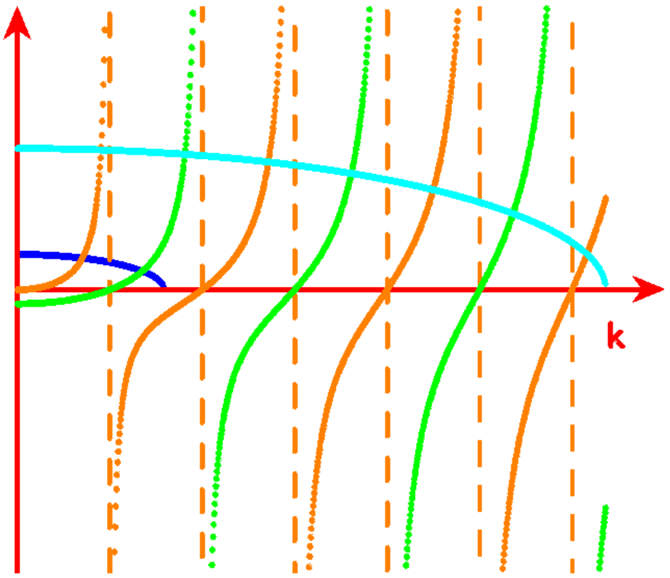
considering the boundary conditions

$$\psi(x=-\infty) = \psi(x=+\infty) = 0 \tag{3.44}$$

as well as conditions at $x = \pm L/2$, i.e. at positions where the potential exhibits the finite discontinuity. We expect to have a continuous probability distribution $\rho(X,t)$ as well as a continous probability current $j(x,t)$ at these points. This leads us to

$$\begin{aligned} \psi(\pm L/2+0) &= \psi(\pm L/2-0) \\ \psi'(\pm L/2+0) &= \psi'(\pm L/2-0) \end{aligned} \tag{3.45}$$

Since the problem is invariant with respect to reflections $x \to -x$ we expect that there are symmetric as well as antisymmetric wave functions. These wave functions are said to possess even (symmetric) and odd (antiysmmetric) parity. In the following we shall explicitly construct these wave functions.



Graphical solution of the equation determining energy eigenstates for a particle in a finite Potential Well.

3.5.2 Solution with even parity:

We first consider the solutions with even parity:

$$\psi(x) = \psi(-x) \tag{3.46}$$

We consider bound states with with energies

$$-U_0 \leq E \leq 0 \tag{3.47}$$

For the following it is convenient to define the quantities κ and k according to

$$\kappa = \sqrt{\frac{2m|E|}{\hbar^2}}$$
$$k = \sqrt{\frac{2m|E| - U_0}{\hbar^2}}$$

The time independent Schrödinger equation can be written as

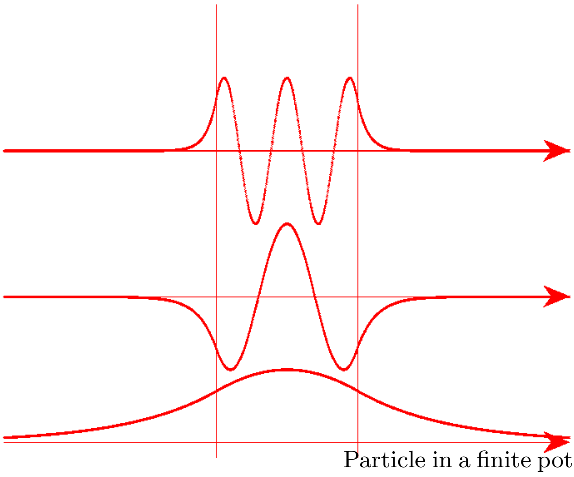
$$\begin{aligned} \frac{d^2}{dx^2}\psi &= \kappa^2\psi \qquad |x| > \frac{L}{2} \\ \frac{d^2}{dx^2}\psi &= -k^2\psi \qquad |x| < \frac{L}{2} \end{aligned} \tag{3.48}$$

and is solved by

$$\begin{aligned} \psi(x) &= A'e^{\kappa x} + A''e^{-\kappa x} \\ \psi(x) &= B' coskx + B'' sinkx \end{aligned} \tag{3.49}$$

The ansatz for the solution with even parity is given by

$$\psi(x) = \begin{array}{ll} Ae^{\kappa(x+L/2)} & x < -L/2 \\ Bcoskx & |x| \leq L/2 \\ Ae^{-\kappa(x-L/2)} & x > L/2 \end{array} \tag{3.50}$$



Particle in a finite potential well: Lowest wave functions with even parity.

The wave function $\psi(x)$ as well as its derivative $\psi'(x)$ has to be continuous at $x = \pm L/2$.

$$A - Bcos\frac{kL}{2} = 0$$
$$-A\kappa + Bksin\frac{kL}{2} = 0 \qquad (3.51)$$

This is a homogeneous set of equations, which can be written in matrix form

$$\begin{pmatrix} 1 & cos\frac{kL}{2} \\ -sin\frac{kL}{2} & 1 \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = 0 \qquad (3.52)$$

The solvability condition reads

$$\frac{k}{\kappa}sin\frac{kL}{2} - cos\frac{kL}{2} = 0 \qquad (3.53)$$

Here, κ as well as k depend on the energy E, which then is determined by the solvability condition. As we shall see from a graphical discussion of this condition there is a finite set of energy values E_i for which the conditions is fullfilled.

For our graphical discussion we introduce $\tilde{\kappa}$ and K according to

$$\tilde{\kappa} = \kappa\frac{L}{2} \qquad , \qquad K = k\frac{L}{2} \qquad (3.54)$$

Using the definition of κ, k we obtain

$$K^2 + \tilde{\kappa}^2 = R^2 = (\frac{L}{2})^2\frac{2mU_0}{\hbar^2} \qquad (3.55)$$

The solvability condition reads:

$$\tilde{\kappa} = ktank = \sqrt{R^2 - k^2} \qquad (3.56)$$

where we have defined

$$R = \frac{L}{2}\sqrt{\frac{2mU_0}{\hbar^2}} \qquad (3.57)$$

The value of k, and, consequently the energy levels, are given by the crossings of the two curves of eq. (3.56). Details can be seen in fig. (3.5.1).

3.5.3 Solution with odd parity:

We now consider solutions with odd parity

$$\psi(x) = -\psi(-x) \qquad (3.58)$$

Again, we consider bound states with energies

$$-U_0 \leq E \leq 0 \qquad (3.59)$$

The ansatz for the solution with odd parity is now given by

$$\psi(x) = \begin{pmatrix} -Ae^{\kappa x} & x < -L/2 \\ Bsinkx & |x| \leq L/2 \\ Ae^{-\kappa x} & x > L/2 \end{pmatrix} \tag{3.60}$$

Thereby the quantities κ and k have been defined above.

The wave function $\psi(x)$ as well as its derivative $\psi'(x)$ has to be continuous at $x = \pm L/2$:

$$\begin{aligned} Ae^{-\kappa L/2} - Bsin\frac{kL}{2} &= 0 \\ -A\kappa e^{-\kappa L/2} - Bkcos\frac{kL}{2} &= 0 \end{aligned} \tag{3.61}$$

As a result we obtain the solvability condition

$$\frac{k}{\kappa}cos\frac{kL}{2} + sin\frac{kL}{2} = 0 \tag{3.62}$$

Again , we can perform a graphical solution of this problem.

To this end we introduce $\tilde{\kappa}$ and K according to

$$\tilde{\kappa} = \kappa\frac{L}{2} \qquad , \qquad K = k\frac{L}{2} \tag{3.63}$$

Using the definition of κ, k we obtain

$$K^2 + \tilde{\kappa}^2 = R^2 = (\frac{L}{2})^2\frac{2mU_0}{\hbar^2} \tag{3.64}$$

The solvability condition reads:

$$-\tilde{\kappa} = kcotk = -\sqrt{R - k^2} \tag{3.65}$$

where we have defined

$$R = \frac{L}{2}\sqrt{\frac{2mU_0}{\hbar^2}} \tag{3.66}$$

Summary: Bound States

Graphically, we can obtain the following results:

- There is at least one solution with even parity $\psi(x) = -\psi(-x)$
- With inreasing value of $|U_0|$, i.e. with increasing depth of the well, the number of energy levels increase. This can be seen from figure (**??**), where it is evident that by increasing U_0,i.e. R, the number of solutions of the transcendental equations increase.
- For large values of U_0, i.e. R, the limiting case of an infinitely deep potential well is approached.

The wave functions have even and odd symmetry, which is clearly a result of the reflectional symmetry of the problem. The wave functions differ with respect to the number of knots. We remind the reader that there is a nonvanishing wave function in the classically forbidden regions. Although this wave function exhibits an exponential decay in this region

$$\psi(x) = ae^{-\frac{x}{d}} \qquad ; \qquad d = \frac{1}{\kappa} \tag{3.67}$$

there is a nonvanishing probability to detect particles in this classically forbidden regions.

3.5.4 Continuous Spectrum

Up to now we have been concerned with particles with energy $E < 0$. In the case of positive energy, we can perform the following ansatz for the wave function

$$\Psi(x,t) = \begin{pmatrix} ae^{ik(x+L/2)} + be^{-ik(x+L/2)} \\ ce^{ik'x} + de^{-ik'x} \\ fe^{ik(x-L/2)} + ge^{-ik(x-L/2)} \end{pmatrix} \tag{3.68}$$

Here,

$$k = \sqrt{\frac{2mE}{\hbar^2}} \qquad , \qquad k' = \sqrt{\frac{2m(E + |U_0|}{\hbar^2}} \tag{3.69}$$

The requirement of continuity of the wave function and the probability current leads to the following set of equations

$$\begin{aligned} a + b &= ce^{-ik'L/2} + de^{ik'L/2} \\ ce^{ik'L/2} + de^{-ik'L/2} &= f + g \\ ik(a - b) &= ik'[ce^{-ik'L/2} - de^{ik'L/2}] \\ ik'(ce^{ik'L/2} + de^{-ik'L/2}) &= ik(f - g) \end{aligned} \tag{3.70}$$

Continuity leads to four equations for six amplitudes $a - g$.

In order to find a solution, we can fix two constants arbitrarily. One constant can be fixed by, e.g. taking $a = 1$. A second choice allos us to construct a *right-running wave* (g=0) or a *left-running wave* (f=0). Furthermore, we see that set of equations determining the amplitudes (**??**) can be fulfilled for arbitrary values of the energy E, in contrast to the case of negative energy discussed above. In this case, the additional requirement that the wave function decays for $x \to \pm\infty$ sets two amplitudes to zero, leading to the linear set of four homogeneous equations for four amplitudes (or, two equations for two coefficients for symmetric and antisymmetric wave functions). As a consequence, a solvability condition has to be fulfilled leading to a discrete set of energy values.

3.6 Reflection at a Barrier: Tunnel Effect

We consider now the motion of a particle in the potential

$$V(x) = \begin{pmatrix} U_0 \; 0 < x < L \\ 0 \quad otherwise \end{pmatrix} \tag{3.71}$$

We assume that a stream of particles with energy $E < U_0$ approaches the potential barrier from the left. The Schrödinger equation in the three regions are

$$\begin{aligned} \frac{\partial^2}{\partial x^2}\psi(x) &= -\kappa^2\psi(x) \qquad x < 0, x > L \\ \frac{\partial^2}{\partial x^2}\psi(x) &= k^2\psi(x) \qquad x < 0, x > L \end{aligned} \tag{3.72}$$

where we have defined

$$\kappa^2 = \frac{2mE}{\hbar^2} \qquad , \qquad k^2 = \frac{2m|E-V|}{\hbar^2} \tag{3.73}$$

3.6.1 $E < V$

In the following we assume that $E < V$:

Using the solutions of these equations in the different regimes we can perform the following ansatz

$$\psi(x) = \{ \begin{matrix} ae^{ikx} + be^{-ikx} \; x < 0 \\ ce^{-\kappa x} + de^{\kappa x} \quad 0 < x < L \\ fe^{ik(x-L)} \end{matrix} \tag{3.74}$$

The time dependent solution would be

$$\Psi(x,t) = \{ \begin{matrix} [ae^{i(kx-\omega t)} + be^{-i(kx+\omega t)}] \; x < 0 \\ ce^{-\kappa x - i\omega t} + de^{\kappa x - i\omega t} \qquad 0 < x < L \\ fe^{i(k(x-L)-\omega t)} \end{matrix} \tag{3.75}$$

where the frequency ω of the wave is related to the (yet unspecified) energy $E = \hbar\omega$. This wave consists of a right- and left running wave in the space $x < 0$, a decaying wave in the classically forbidden regime $0 < x < L$ and a rightrunning wave in the regime $x > L$. We remind the reader that, in the classical description, a particle would not be able to traverse the potential barrier and would be reflected. A quantum mechanical particle can tunnel through the barrier, provided there is a nonvanishing amplitude c of the rightrunning wave.

In order to describe a beam of particles moving from $x = -\infty$ towards the barrier, we evaluate the probability current

$$j = \frac{\hbar}{2mi}[\Psi(x,t)^* \frac{\partial}{\partial x}\Psi(x,t) - \Psi(x,t)\frac{\partial}{\partial x}\Psi(x,t)^*] \tag{3.76}$$

We explicitly obtain

$$\begin{aligned} j &= \begin{pmatrix} \frac{\hbar k}{2mi}[(a^* e^{-ikx} + b^* e^{ikx}) ik(ae^{ikx} - be^{-ikx}) - c.c.] \\ \frac{\hbar}{2mi}[(c^* e^{-\kappa x} + d^* e^{\kappa x})(-\kappa)(ce^{-\kappa x} + d^* e^{\kappa x}) - c.c.] \\ \frac{\hbar}{2mi}[f^* e^{-ikx} ikf e^{ikx} - c.c.] \end{pmatrix} \\ &= \begin{pmatrix} \frac{\hbar k}{m}(|a|^2 - |b|^2) \\ \frac{\kappa}{m} i[d^* c - dc^*] \\ \frac{\hbar k}{m}|f|^2 \end{pmatrix} \end{aligned} \tag{3.77}$$

Continuity of the current yields

$$|a|^2 - |b|^2 = |f|^2 \tag{3.78}$$

We define the reflection coefficient R and the transmission coefficient T according to

$$R = \frac{|b|^2}{|a|^2} \quad , \quad T = \frac{|f|^2}{|a|^2} \tag{3.79}$$

with the relationsship

$$R + T = 1 \tag{3.80}$$

In case where $T > 0$ particles can be detected behind the barriers, also in the case where $E < V$. Classically the particles would be reflected in this case, $R = 1$. A nonvanishing transmission coefficient T indicates that quantum particles can penetrate through a potential barrier. This effect is denoted as *tunneling*.

Let us now determine the transmission and reflection coefficiennt explicitly. The amplitudes a, aR as well as the corresponding energy values are determined from the boundary conditions. Again, we have to require continuity of the wave function, as well as the spatial derivative of the wave function at the boundaries $x = 0$, $x = L$.

Continuity of the wave function $\psi(x)$ at $x = 0, L$ yields the relationships

$$\begin{aligned} a + b &= c + d \\ ce^{-\kappa L} + de^{\kappa L} &= f \end{aligned} \tag{3.81}$$

Continuity of the derivative of the wave function $\psi'(x)$ at $x = 0, L$ yields

$$\begin{aligned} ik(a - b) &= -\kappa c + \kappa d \\ -\kappa ce^{-\kappa L} + \kappa de^{\kappa L} &= ikf \end{aligned} \tag{3.82}$$

There are 4 equations for 5 coefficients. We can fix the amplitude of the incoming wave $a = 1$. Since the amplitudes a, b are the amplitudes of an incoming wave and the reflected wave we can make the ansatz $b = ra$ with a factor r, which describes the reflection. Furthermore, we are able to out $a = 1$, normalizing the amplitude of the incoming wave to $a = 1$. As a consequence, we obtain the following inhomogeneous set of linear equations

$$\begin{aligned} r - c - d &= -1 \\ ce^{-\kappa L} + de^{\kappa L} - f &= 0 \\ r + \frac{i\kappa}{k}c - \frac{i\kappa}{k}d &= 1 \\ ce^{-\kappa L}\frac{i\kappa}{k} - de^{\kappa L}\frac{i\kappa}{k} - f &= 0 \end{aligned} \tag{3.83}$$

In order to calculate the coefficients, we separate the set of equations into

$$\begin{aligned} c(1+i\alpha) + d(1-i\alpha) &= 2 \\ ce^{-\kappa L}(1-i\alpha) + de^{\kappa L}(1+i\alpha) &= 0 \end{aligned} \tag{3.84}$$

and

$$\begin{aligned} r &= (c+d) - 1 \\ t &= ce^{-\kappa L} + de^{\kappa L} \end{aligned} \tag{3.85}$$

We obtain by defining

$$\alpha = \frac{\kappa}{k} \tag{3.86}$$

$$d = -ce^{-2\kappa L}\frac{1-i\alpha}{1+i\alpha} \tag{3.87}$$

$$c = 2\frac{1+i\alpha}{(1+i\alpha)^2 - (1-i\alpha)^2 e^{-2\kappa L}} \tag{3.88}$$

$$\begin{aligned} t &= \frac{4i\alpha e^{-\kappa L}}{(1+i\alpha)^2 - (1-i\alpha)^2 e^{-2\kappa L}} \\ &= \frac{2i\alpha}{(1-\alpha^2)sinh\kappa L + 2i\alpha cosh\kappa L} \\ &= \frac{1}{cosh\kappa L - \frac{1-\alpha^2}{2\alpha} isinh\kappa L} \end{aligned} \tag{3.89}$$

We can now state our result for the transmission coefficient T

$$T = |t|^2 = \frac{1}{cosh^2\kappa L + \frac{(1-\alpha^2)^2}{4\alpha^2}sinh^2\kappa L} = \frac{4\alpha^2}{4\alpha^2 + (1+\alpha^2)^2 sinh^2\kappa L} \tag{3.90}$$

whereas the reflection coefficient is just obtained from

$$R = T - 1 \tag{3.91}$$

3.6.2 $E > V$

If we consider the case of particles with energy larger as V, the potential height of the barrier, classical particles will all pass the barrier. Quatum particles, however, feel the barrier indicating that there is a nonvanishing transmission coefficient.

This transmission coefficient can easily be calculated by noticing that all formulas remain valid, except that we now have to consider that κ is imaginary, since $E > V$:

$$\kappa = i\tilde{\kappa} \qquad \alpha = i\tilde{\alpha} \tag{3.92}$$

The transmission coefficient reads:

$$T = |t|^2 = \frac{4\tilde{\alpha}^2}{4\tilde{\alpha}^2 + (1-\tilde{\alpha}^2)^2 sin^2 \tilde{\kappa} L} \tag{3.93}$$

3.6.3 Wave Packets

Up to now we have considered a monochromatic incoming wave. In order to describe a beam of localized moving towards the barrier, one has to bild up wave packets.

The wave packet on the left side and right hand side of the barrier has the form

$$\Psi(x,t) = \begin{pmatrix} \int dka(k) e^{ikx_0} e^{-i\omega(k)t} [e^{ikx} + r(k) e^{-ikx} \\ \int dka(k) e^{ikx_0} e^{-i\omega(k)t} [c(k) e^{-\kappa x} + d(k) e^{\kappa x}] \\ \int dka(k) e^{ikx_0} e^{-i\omega(k)t} t(k) e^{ikx} \end{pmatrix} \tag{3.94}$$

where

$$\omega(k) = \frac{\hbar k^2}{2m} \tag{3.95}$$

The amplitude $a(k)$ of the wave packet can be, e.g. taken as a Gaussian

$$a(k) = \frac{1}{\sqrt{2\pi Q}} e^{-\frac{(k-k_0)^2}{2Q}} \tag{3.96}$$

3.7 Wave Mechanics in Two Dimensions

3.7.1 Quantum Dots

3.7.2 Quantum Billards

4

Hilbert Space

4.1 Linear Space

We consider vectors $|\psi_i >$, which can be added, $|\psi_1 > +|\psi_2 >$ and multiplied by a scalar quantity α, $|\psi >= \alpha|\psi_1 >$. The set of vectors form a *linear space*, provided the following axioms are fullfilled:

a) Neutral element $\vert 0 >$	$\vert\psi > +\vert 0 >= \vert\psi >$
b) Inverse element	$\vert\psi > +\vert -\psi >= \vert 0 >$
c) Associativity	$\vert\psi_1 > +(\vert\psi_2 > +\vert\psi_3 >) = (\vert\psi_1 > +\vert\psi_2 >) + \vert\psi_3 >$
d) Distributivity	$\vert\alpha(\psi_1 + \psi_2) >= \alpha\vert\psi_1 > +\alpha\vert\psi_2 >$
e)	$\vert(\alpha + \beta)\psi >= \alpha\vert\psi > +\beta\vert\psi >$
f)	$\vert(\alpha\beta)\psi >= \alpha\vert\beta\psi >$
g)	$\vert 1\psi >= \vert\psi >$

4.2 Normed Linear Space

A linear space is extended to a *normed linear space* if to each element ψ there is a positive real number $||\psi||$ obeying the following axioms

a) Positivity	$\|\|\psi\|\| > 0$
b) Neutral element	$\|\|0\|\| = 0$
c)	$\|\|\alpha\psi\|\| = \|\alpha\|\|\|\psi\|\|$
d) Triangle inequality	$\|\|\psi_1 + \psi_2\|\| \leq \|\|\psi_1\|\| + \|\|\psi_2\|\|$

4.2.1 Scalar Product

A norm in a linear space can be defined via a *scalar product.* The scalar product is denoted as

$$< \psi_1|\psi_2 > \tag{4.1}$$

and can be a complex quantity obeying the following axioms

a)	$< \psi_3\|(\psi_1 + \psi_2) >=< \psi_3\|\psi_1 > + < \psi_3\|\psi_2 >$
b)	$< \psi_1\|\alpha\psi_2 >= \alpha < \psi_1\|\psi_2 >$
c)	$< \psi_1\|\psi_2 >=< \psi_2\|\psi_1 >^*$
d)	$< \psi\|\psi >\geq 0$
e)	$< \psi\|\psi >= 0$ implies $\psi = 0$

The scalar product can be used to define a norm

$$||\psi|| = \sqrt{< \psi|\psi >} \tag{4.2}$$

Frequently, the scalar product is denoted as *inner product.* A linear space with a scalar product is an *inner product space.*

4.2.2 Schwarz Inequality

A scalar product obeys the Schwarz inequality:

$$| < \psi_1|\psi_2 > | \leq ||\psi_1|| \; ||\psi_2|| \tag{4.3}$$

For a proof we start from the inequality

$$||(\psi_1 - \alpha\psi_2)||^2 \geq 0 \tag{4.4}$$

which implies

$$||\psi_1||^2 - \alpha < \psi_1|\psi_2 > -\alpha^* < \psi_2|\psi_1 > +|\alpha|^2||\psi_2||^2 \geq 0 \tag{4.5}$$

Now we choose

$$\alpha = \frac{< \psi_2|\psi_1 >}{< \psi_2|\psi_2 >} \tag{4.6}$$

and end up with the inequality of Schwarz.

4.2.3 Orthogonal Vectors

Two vectors are orthogonal with respect to each other if the scalar product

$$< \psi_1|\psi_2 >= 0 \tag{4.7}$$

vanishes

4.2.4 Completeness

A normed linear space is complete, if each convergent Cauchy sequence $|\psi_n >$ has a limit which belongs to this space. A sequence of vectors $\psi_n >$ is convergent, provided

$$||(\psi_n - \psi_{n+N})|| \leq \epsilon(n) \tag{4.8}$$

4.3 Hilbert Space

A Hilbert space is a complete linear space with a scalar product. It is also denoted as *inner product space*.

4.4 Basis, Dimension, Completeness

In a Hilbert space, we can choose a set of basis vectors denoted by

$$|\psi_1 >, |\psi_2 >, ... \tag{4.9}$$

The vector

$$|\psi >= \sum_i c_i|\psi_i > \tag{4.10}$$

yields a new vector, which is an element of the Hilbert space.

We can consider an *orthogonal set* of basis vectors, which obey the orthogonality condition

$$< \psi_i|\psi_j >= \delta_{ij} \tag{4.11}$$

An orthogonal basis can be constructed iteratively using the Schmidt orthogonalization procedure: From the set $|\tilde{\psi_1}>, |\tilde{\psi_2}>$ we form

$$\begin{aligned}
|\psi_1> &= |\tilde{\psi_1}> \\
|\psi_2> &= |\tilde{\psi_2}> - <\tilde{\psi_2}|\psi_1>|\psi_1> \\
|\psi_3> &= .....
\end{aligned} \tag{4.12}$$

A basis $|\psi_i>$ is complete provided each vector of the space can be represented as a linear superposition of basis vectors

$$|\psi>=\sum_i c_i|\psi_i> \tag{4.13}$$

the coefficients are the scalar products

$$c_i =<\psi_i|\psi> \tag{4.14}$$

Forming the scalar product

$$<\psi_i|\psi>=<\psi_i|\sum_j c_j\psi_j>=\sum_j c_j<\psi_i|\psi_j>=c_i \tag{4.15}$$

Inserting this expression into (**??**) we obtain

$$|\psi>=\sum_i|\psi_i>c_i=\sum_i|\psi_i><\psi_i|\psi> \tag{4.16}$$

which we rewrite in the form

$$1=\sum_i|\psi_i><\psi_i| \tag{4.17}$$

The quantity $\psi_1><\psi_2|$ is denoted as *dyadic product.*

The *dimension of a Hilbert space* is the number of basis vectors necessary to expand each vector of the space. The space is *separable* if the there is a countable set of basis vectors. The number of basis vectors can be infinite.

4.5 Examples

4.5.1 Euclidean Space

The real vectors $\mathbf{a}=[a_1,a_s,..a_N]$ in R^n with the scalar product

$$<\mathbf{a}|\mathbf{b}>=\sum_{i=1}^N a_ib_i \tag{4.18}$$

form a Hilbert space, the euclidean space.

4.5.2 Space of periodic functions

Our next example is the set of functions $\varphi(x)$ which are *periodic* in x with period L and are *square integrable*. This means that the integrals

$$\int dx|\psi(x,t)|^2 < \infty \tag{4.19}$$

These functions form a linear space with respect to addition $\psi_1(x) + \psi_2(x)$ and multiplication with a scalar, $\alpha\psi(x)$.

The scalar product is defined by the integral

$$< \psi_1|\psi_2 >= \int_0^L dx\psi_1(x)^*\psi_2(x) \tag{4.20}$$

These functions can expanded into a Fourier-series:

$$f(x) = \sum_{n=-\infty}^{\infty} c_n \frac{1}{\sqrt{L}} e^{in\frac{2\pi}{L}x} \tag{4.21}$$

The set of functions

$$|\varphi_n >= \frac{1}{\sqrt{L}} e^{ink_0x} \qquad n = -\infty, ..., \infty \qquad k_0 = \frac{2\pi}{L} \tag{4.22}$$

form a orthonormal set of basis functions. This follows from the straightforward evaluation of

$$< \varphi_n|\varphi_m >= N^2 \int_0^L dxe^{i(m-n)k_0x} = N^2\delta_{nm}L \tag{4.23}$$

The Fourier-coefficients can be calculated by the integral

$$c_n = \int_0^L \frac{1}{\sqrt{L}} e^{-ink_0x}\psi(x) \tag{4.24}$$

The Fourier representation yields

$$\Psi(x) = \sum_n \int_0^L dx'\varphi_n(x')^*\Psi(x')\varphi_n(x) \tag{4.25}$$

which leads us to the *completeness relation*

$$\delta(x - x') = \sum_n \int_0^L dx'\varphi_n(x')^*\varphi_n(x) \tag{4.26}$$

We explicitly see that the δ-function can be represented in terms of the basis function.

4.5.3 Square Integrable Functions

We consider the space of complex functions $\psi(x)$, for which the integrals

$$\int_{-\infty}^{\infty} dx|\psi(x)|^2 < \infty \tag{4.27}$$

exist. These functions are denoted as *square integrable functions*.

The square integrable functions form a linear space with respect to the addition and multiplication with a complex variable α:

$$\psi_1(x) + \psi_2(x) = \psi(x) \tag{4.28}$$

The sum $\psi(x)$ is again square integrable, since

$$|\psi(x)|^2 = |\psi_1(x) + \psi_2(x)|^2 \leq |\psi_1(x)|^2 + |\psi_2(x)|^2 \tag{4.29}$$

so that

$$\int_{-\infty}^{\infty} dx|\psi(x)|^2 < \int_{-\infty}^{\infty} dx|\psi_1(x)|^2 + \int_{-\infty}^{\infty} dx|\psi_2(x)|^2 < \infty \tag{4.30}$$

For square integrable functions the scalar product can be defined by the integral

$$< \psi_1|\psi_2 >= \int dx \psi(x)_1^* \psi_2(x) \tag{4.31}$$

The property e) has to be discussed in some more detail. The space of square integrable functions may contain functions, which are zero on a space of Lebesque measure zero. An example is the function

$$\begin{aligned} u(x) &= 1 \qquad forx = 0 \\ u(x) &= 0 \qquad otherwise \end{aligned} \tag{4.32}$$

The (Lesbeque) integral of this function is zero,

$$\int_{-\infty}^{\infty} dx u(x) = 0 \tag{4.33}$$

Thus, in principle, the property e) is not fullfilled. However, if we consider the equivalence class of functions which differ from each other by functions which are different from zero on sets of measure zero, the property e) is fullfilled and (4.31) defines a scalar product in the space of the square integrable functions.

4.5.4 Square Integrable Functions in N Dimensions

Generalization to three, N dimensions:

$$\int d^3\mathbf{x}|\psi(\mathbf{x})|^2 \leq \infty \tag{4.34}$$

4.6 Linear Operators

Several times we have encountered operators. An operator A transforms an element of a Hilbert space into another element of this space:

$$|\Psi_2 >= \hat{A}|\Psi_1 > \tag{4.35}$$

4.6.1 Example: Euclidean Space

In the Euclidean space the operators $\hat{A}$ are represented by matrices. It turns a vector $|\Psi_1 >$ into a vector $|\Psi_2 >$. If we take a basis $|\varphi_i >$ we can expand the vectors

$$|\Psi_1 >= \sum_{i=1}^{N} a_i|\varphi_i > \qquad , \qquad |\Psi_2 >= \sum_{i=1}^{N} b_i|\varphi_i > \tag{4.36}$$

we obtain

$$\sum_{i=1}^{N} b_i|\varphi_i >= A\sum_{i=1}^{N} b_i|\varphi_i >= \sum_{i=1}^{N} b_i A|\varphi_i > \tag{4.37}$$

Taking the scalar product we obtain the representation of the operator A in terms of the matrix

$$b_i = \sum_{j=1}^{N} A_{ij} a_j \tag{4.38}$$

with

$$A_{ij} =< \varphi_i|A|\varphi_j > \tag{4.39}$$

4.6.2 Example: Complex Space

4.6.3 Example: Position and Momentum Operator

Examples of physically relevant opertors are the position and momentum operator $\hat{x}$, $\hat{p}$.

4.7 Adjoint Operator, Hermitian Operator

We shall now define the adjoint operator $A^\dagger$ by the relation

$$< \Psi_1|\hat{A}|\Psi_2 >=< \hat{A}^\dagger \Psi_1|\Psi_2 > \tag{4.40}$$

A *selfadjoint operator* is defined by the relationship

$$\hat{A} = \hat{A}^\dagger \tag{4.41}$$

The operator need not be defined for all vectors of the Hilbert space. It may only be defined on a subset D of H.

A selfadjoint operator is an *hermitian opertor* if $D^\dagger = D$.

4.7.1 Momentum Operator

The momentum operator is an hermitian operator

$$< \Psi_1(x)|\frac{\hbar}{i}\frac{\partial}{\partial x}|\Psi_2(x) >=< \frac{\hbar}{i}\frac{\partial}{\partial x}\Psi_1(x)|\Psi_2(x) > \tag{4.42}$$

Proof: We explicitly write down the scalar products in terms of th integrals

$$\begin{aligned} < \psi_1(x)|\hat{p}|\psi_2 > &= \int dx \psi_1(x)^* \frac{\hbar}{i}\frac{\partial}{\partial x}\psi_2(x) \\ &= -\int dx \left(\frac{\hbar}{i}\psi_1(x)\right)^* \frac{\partial}{\partial x}\psi_2(x) \\ &= \left[-\left(\frac{\hbar}{i}\psi_1(x)\right)^* \psi_2(x)\right]_{-\infty}^{\infty} \\ &= \int dx \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\psi_1(x)\right)^* \psi_2(x) =< \hat{p}\psi_1|\psi_2 > \end{aligned} \tag{4.43}$$

4.7.2 Operator of Kinetic Energy

$$< \Psi_1(x)| -\frac{\hbar^2}{2m}\Delta|\Psi_2(x) >=< -\frac{\hbar^2}{2m}\Delta\Psi_1(x)|\Psi_2(x) > \tag{4.44}$$

4.7.3 Hamilton Operator

The Hamilton operator is an hermitian operator:

$$\hat{H} = \frac{(\hat{p})^2}{2m} + U(\hat{x}) = \hat{H}^\dagger \tag{4.45}$$

4.8 Eigenvalue Problems

Eigenvalue problem

$$\hat{A}|\psi >= \lambda|\psi > \tag{4.46}$$

The eigenvalue problem connected with a linear operator $\hat{A}$ in general has a nontrivial solution only for a certain set of *eigenvalues* λ_i.

4.8.1 Example: Euclidean Space

In Euclidean space R^N the operators are matrices. Therefore, there are N eigenvalues which are the roots of the so-called *characteristic equation*

$$Det[A - \lambda E] = 0 \tag{4.47}$$

4.8.2 Example: Momentum Operator

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\psi(x) = \lambda|\psi(x)> \tag{4.48}$$

We consider the space of squar integrable periodic functions. The eigenfunctions are given by

$$|\psi_k >= \frac{1}{\sqrt{L}}e^{ikx} \tag{4.49}$$

and the eigenvalues are

$$\lambda_k = \hbar k \tag{4.50}$$

4.9 Hermitian Operators

The eigenvalues of hermitian operators are real. The set of eigenvalues of an operator is denoted as the *spectrum* of A
Proof:

$$< \Psi|A|\Psi >= \lambda < \Psi|\Psi >=< A\Psi|\Psi >= \lambda^* < \Psi|\Psi > \tag{4.51}$$

The eigenfunctions ψ_1 and ψ_2 of a selfadjoint operator belonging to different eigenvalues are *orthogonal*:
Proof:

$$< \psi_1|A|\psi_2 >= \lambda_2 < \psi_1|\psi_2 >= \lambda_1 < \psi_1|\psi_2 > \tag{4.52}$$

For the case $\lambda_1 \neq \lambda_2$ we conclude

$$< \psi_1|\psi_2 >= 0 \tag{4.53}$$

In case of a degeneracy of an eigenvalue, i.e. in case that there are two or more eigenvectors belonging to a single eigenvalue, we can orthogonalize these vectors.

The eigenvectors of a hermitian operator form a complete orthogonal set:

$$\begin{aligned} < \psi_i|\psi_j > &= \delta_{ij} \\ \sum_i |\psi_i >< \psi_i| &= 1 \end{aligned} \tag{4.54}$$

4.9.1 Projection Operator

We can take

$$P = \frac{|\psi_1 >< \psi_1|}{||\psi_1||} \tag{4.55}$$

$$P^2 = P \tag{4.56}$$

4.9.2 Spectral Decomposition

4.10 Functions of Operators

It is possible to define functions of an operator $\hat{A}$, $\hat{F}(\hat{A})$. It is straightforward to define the operators $\hat{A}^2$, $\hat{A}^n$. Provided the function $F(a)$ has a representation in terms of a Taylor series with coefficients F_k we are able to define the operator function according to

$$\hat{F}(\hat{A}) = \sum_k F_k (\hat{A})^k \tag{4.57}$$

An example is the matrix exponential of an operator $\hat{A}$

$$e^{\hat{A}} = \sum_{k=0} \frac{1}{k!} (\hat{A})^k \tag{4.58}$$

4.11 Commuting, Noncommuting Operators

We consider the product of two operators, $\hat{A}\hat{B}$, and compare it to the product $\hat{B}\hat{A}$. In general, these operators are different.

4.11.1 Position, Momentum

As an example we consider the operators $A = \hat{x}$, B=$\hat{p}$

$$\begin{aligned} \hat{x}\hat{p} &= x \frac{\hbar}{i} \frac{\partial}{\partial x} \\ \hat{p}\hat{x} &= \frac{\hbar}{i} \frac{\partial}{\partial x} x \end{aligned} \tag{4.59}$$

In order to compare both expressions we have to consider e.g. the quantity

$$\begin{aligned} \hat{p}\hat{x}|\psi> &= \frac{\hbar}{i} \frac{\partial}{\partial x} (x\psi(x)) \\ &= x \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x) + \frac{\hbar}{i} \psi(x) = \hat{x}\hat{p} + \frac{\hbar}{i} \end{aligned} \tag{4.60}$$

where we have made use of the product rule of differentiation. We can now define the difference between the operators $\hat{x}\hat{p}$ and $\hat{p}\hat{x}$

$$\hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar \tag{4.61}$$

4.11.2 Definition: Commutator

Let us now generalize: We define the commutator $[A, B]$ of two operators A, B by the difference of the product AB and BA:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{4.62}$$

4.11.3 Eigenvectors of Commuting Operators

Two commuting operators $\hat{A}$, $\hat{B}$ have common eigenvectors. For the proof we consider the eigenvalue equation

$$\hat{A}|\varphi_i >= \lambda_i|\varphi > \tag{4.63}$$

From the relation

$$\hat{B}\hat{A}|\varphi_i >= \hat{A}\hat{B}|\varphi_i >= \lambda_i\hat{B}|\varphi > \tag{4.64}$$

we conclude that $B|\varphi_i >$ is an eigenvector of A with eigenvalue λ_i. We assume that the eigenvalue is simple, then

$$\hat{B}|\varphi_i >= \gamma_i|\varphi_i > \tag{4.65}$$

which shows that the vector $|\varphi_i >$ is also an eigenvector of the operator $\hat{B}$.

4.11.4 Functions of Commuting Operators

Operator functions of commuting operators commute.

4.12 Uncertainty Relations

We start from Schwarz inequality

$$< \Psi_1|\Psi_1 >< \Psi_2|\Psi_2 > \quad \geq \quad | < \Psi_1|\Psi_2 > |^2 \tag{4.66}$$

which is valid for each pair of elements of a Hilbert space. We consider two Hermitian operators A, B. We define by

$$\begin{aligned} |\Psi_1 >&= \hat{A}|\Psi > \\ |\Psi_2 >&= \hat{B}|\Psi > \end{aligned} \tag{4.67}$$

and obtain using the Schwarz inequality and the property, the A, B are Hermitian operators

$$\begin{aligned} &< \Psi|\hat{A}^2|\Psi >< \Psi|\hat{B}^2|\Psi > \\ &\geq | < \Psi|\hat{A}\hat{B}|\Psi > |^2 \end{aligned} \tag{4.68}$$

We introduce the abbreviation

$$z =< \Psi|\hat{A}\hat{B}|\Psi > \tag{4.69}$$

and use the estimate

$$|z|^2(Rez)^2 + (Imz)^2 \geq (Imz)^2 = (\frac{z - z^*}{2i})^2 \tag{4.70}$$

Since

$$z =< \mathit{\Psi}|\hat{A}\hat{B}|\mathit{\Psi} >=< \hat{B}\hat{A})\mathit{\Psi}|\mathit{\Psi} > \tag{4.71}$$

and, using the assumption that $\hat{A}$, $\hat{B}$ are hermitian operators, we obtain

$$z^* =< \mathit{\Psi}|\hat{B}\hat{A}|\mathit{\Psi} > \tag{4.72}$$

as well as

$$\begin{aligned} \frac{z - z^*}{2i} &= \frac{1}{2i} < \mathit{\Psi}|\hat{A}\hat{B} - \hat{B}\hat{A}|\mathit{\Psi} > \\ &= \frac{1}{2i} < \mathit{\Psi}|[\hat{A}, \hat{B}]|\mathit{\Psi} > \end{aligned} \tag{4.73}$$

where we have introduced the commutator $[\hat{A}, \hat{B}]$ of $\hat{A}$ and $\hat{B}$.

As a consequence, we obtain the general *uncertainty relationship* between two operators $\hat{A}$, $\hat{B}$

$$\mathit{\Delta} A \mathit{\Delta} B \geq \frac{1}{2}| < \mathit{\Psi}|[A, B]|\mathit{\Psi} > | \tag{4.74}$$

Thereby, we have defined the uncertainties

$$\mathit{\Delta} A = \sqrt{< \mathit{\Psi}|(A- < A >)^2|\mathit{\Psi} >} \qquad , \qquad \mathit{\Delta} B = \sqrt{< \mathit{\Psi}|(B- < B >)^2|\mathit{\Psi} >} \tag{4.75}$$

4.12.1 Uncertainty Relation

The commutator between the operators $\hat{x}$ and $\hat{p}$ is

$$[\hat{x}, \hat{p}] = i\hbar \tag{4.76}$$

Consequently, we obtain the uncertainty relation

$$\mathit{\Delta} x \mathit{\Delta} p \geq \frac{\hbar}{2} \tag{4.77}$$

5

Chance and Probability

Probability theory has been developed to cope with random events. Diffraction experiments with quantum particles like electrons, neutrons have demonstrated the random outcome of a single event as well as the emergence of well-predictable interference patterns.

An operational approach has been developed in order to deal with systems with random outcomes. It is based on the notion of the probability p_i of a random event denoted as ω_i. The *elementary events* ω_i belong to a set Ω, which is denoted as *sample space*. The probability p_i is operationally defined as the number

$$p_i = lim_{N \to \infty} \frac{N_i}{N} \tag{5.1}$$

Thereby, N denotes a number of experiments, and N_i counts the number of these experiments in which the event ω_i has been realized. The probability, therefore, can be measured by performing a large number of experiments.

5.1 Probability

Our operational definition of probability immediately implies that the probability p_i is normalized:

$$\sum_i p_i = \sum_i lim_{N \to \infty} \frac{N_i}{N} = 1 \tag{5.2}$$

The sum is over all elementary events.

5.2 Probability Density

For the case of a continuous random variable we expect that the probability $p(x, dx)$ is proportional to the width dx of the interval:

$$p(x, dx) = \rho(x)dx \tag{5.3}$$

This defines the probability density $\rho(x)$. This probability density is normalized

$$\int \rho(x)dx = 1 \tag{5.4}$$

5.3 Expectations

The introduction of the notion of probability allows one to calculate expectation values of random quantities and, in turn, allows one to perform predictions about the outcome of experiments with random variables.

The mean value of a quantity is given by

$$< x >= \sum_i x_i p_i = \int \rho(x)xdx \tag{5.5}$$

Accordingly, we can define expectations of the quantities x^2, x^n which are denoted as moments:

$$< x^n >= \sum_i x_i^n p_i = \int \rho(x)x^n dx \tag{5.6}$$

An important quantity is the variance defined as

$$< x^2 > - < x >^2 \tag{5.7}$$

5.4 Mathematical Definition of Probability

The notion of probability requires a mathematical definition. We shall briefly outline this definition, which is based on the notion of a sample space Ω. The sample space consists of sets Ω_i including the empty set 0. ......

6

Concepts of Quantum Physics

The behaviour of a quantum system is described by a time dependent state vector

$$|\Psi(t)> \tag{6.1}$$

which is element of a Hilbert space H. This state vector is normed, i.e.

$$||\Psi|| = \sqrt{\langle\Psi(t)|\Psi(t)\rangle} \tag{6.2}$$

The wave function contains all information on the quantum system.

The spatio-temporal evolution is given by the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)> = \hat{H}|\Psi(t)> \tag{6.3}$$

Here, $\hat{H}$ denotes the Hamilton operator.

6.1 Axiomatic Quantum Theory

- Physical states are elements of a complex Hilbert space.
- Physical observables are Hermitian operators defined in this Hilbertspace.

  Measurements are interpreted in a probabilistic sense. The expectation value of a physical variable is given by the scalar product

  $$< \hat{A} > = < \Psi|A|\Psi > \tag{6.4}$$

- Temporal Evolution

  The temporal evolution of the state vector is determined by the Schrödinger equation

  $$i\hbar\frac{\partial}{\partial t}|\Psi(t)> = \hat{H}|\Psi(t)> \tag{6.5}$$

For a particle the Hamilton operator is obtained from the classical Hamilton function

$$H = \frac{\hat{p}^2}{2m} + \hat{U}(\hat{x}) \tag{6.6}$$

- Measurement Process
  A measurement of an observable A yields one of the eigenvalues of the corresponding operator $\hat{A}$.

Observable	Operator
Position	$\hat{x} = x$
Momentum	$\hat{p} = \frac{\hbar}{i}\nabla$
Kinetic Energy	$\hat{T} = -\frac{\hbar^2}{2m}\Delta$
Potential Energy	$\hat{U}(\hat{x}))$

6.2 Physical Observables and Hermitian Operators

To each physical observable A we assign an Hermitian operator $\hat{A}$. The measured values of the observable are the eigenvalues a_i of the operator in Hilbert space defined by the eigenvalue problem

$$\hat{A}|\varphi_i^A >= a_i|\varphi_i^A > \tag{6.7}$$

Since the operator $\hat{A}$ is Hermitian, the eigenvalues are real numbers. The number of the eigenvalues equals the dimension of the Hilbert space.

Since the operator $\hat{A}$ is an Hermitian operator, it has a complete set of orthonormal eigenstates:

$$< \varphi_i^A|\varphi_j^A > = \delta_{ij}$$
$$\sum_i |\varphi_i^A >< \varphi_i^A| = 1 \tag{6.8}$$

6.3 Probabilistic Interpretation

The state vector $|\Psi(t) >$ has to be interpreted in a statistical sense.

We represent the state vector $|\Psi(t) >$ in terms of the eigenfunctions $|\varphi_j^A >$ of $\hat{A}$:

$$|\Psi(t)>=\sum_i c_i(t)|\varphi_i^A> \tag{6.9}$$

The expectation of the observable $\hat{A}$ can then be evaluated according to

$$\begin{aligned}\langle\hat{A}\rangle = <\Psi(t)|\hat{A}|\Psi(t)> &= \sum_j\sum_k c_j^* c_k \lambda_k^A <\varphi_j^A|\varphi_k^A> \\ &= \sum_j |c_j(t)|^2 \lambda_k^A \end{aligned} \tag{6.10}$$

This expression has to be interpreted in a probabilistic sense: The physical observable A has the set of eigenvalues λ_k, which contribute to the expectation $<\Psi(t)|\hat{A}|\Psi(t)>$ with $|c_j(t)|^2$.

A prediction of the outcome of a quantum mechanical experiment, therefore, has to assign a probability $|c_j(t)|^2$ to the measurement of the eigenvalue λ_j^A.

6.4 Measurement Process

In a double slit experiment it is not possible to predict the location where a single particle will hit the screen with certainty. Shortly after the particle has hit the screen, however, it can be definitely localized. Only predictions on probabilities of the outcome of an experiment are possible. The outcome of a measurement of a physical observable is uncertain, after measurement it is certain. This fact has to be incorporated into a quantum theory and is frequently denoted as the *collapse of the wave function.*

We consider a quantum system described by the state vector $\Psi(t)>$. We intend to measure a physical quantity represented by the Hermitian operator $\hat{A}$. The possible outcomes of the measurement our the set of eigenvalues a_i with corresponding eigenstates $|\varphi_i^a>$. A decomposition of the state vector yields

$$|\Psi(t)>=\sum_i c_i(t)|\varphi_i^A> \tag{6.11}$$

The probability, to measure the value a_i is given by

$$p_i = |c_i(t)|^2 \tag{6.12}$$

The knowledge of p_i allows one to make statistical predictions.

After the measurement, where we definitely measure the value a_j we know that the state vector is

$$|Psi(t+0)>=|\varphi_j^a> \tag{6.13}$$

Therefore, the measurement changes the state vector from

$$\Psi(t-0)>=\sum_i c_i(t)|\varphi_i^a>\to|\Psi(t+0)>=|\varphi_j^a> \tag{6.14}$$

This property of a quantum system is denoted as the *collapse of the state vector.*

7

Harmonic Oscillators

7.1 Classical Harmonic Oscillator

We shall briefly reconsider the treatment of a harmonic oscillator in classical mechanics.

7.1.1 Hamilton Function

The Hamilton function reads

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2} q^2 \tag{7.1}$$

and the canonical equations read

$$\begin{aligned} \dot{q} &= \frac{\partial}{\partial p} H(p,q) = \frac{p}{m} \\ \dot{p} &= -\frac{\partial}{\partial p} H(p,q) = -m\omega^2 q \end{aligned} \tag{7.2}$$

Elimination of the momentum p yields a second order differential equation

$$\ddot{q} + \omega^2 q = 0 \tag{7.3}$$

The solution reads

$$\begin{aligned} q(t) &= A sin \omega t + B cos \omega t \\ p(t) &= A \frac{\omega}{m} sin \omega t + B \frac{\omega}{m} cos \omega t \end{aligned} \tag{7.4}$$

7.1.2 Phase Space

One can represent the instantaneous classical state of an oscillator by the specification of $[q(t), p(t)]$. Therefore, the temporal evolution can be viewed by the evolution of this point in *phase space* spanned by the coordinates q, p. The energy is a constant and the trajectorie of an oscillator is an ellipse

$$1 = \frac{p^2}{2mE} + \frac{m\omega^2 q^2}{2E} \tag{7.5}$$

with the semi axis

$$\begin{aligned} a &= \sqrt{\frac{2E}{m\omega^2}} \\ b &= \sqrt{2mE} \end{aligned} \tag{7.6}$$

7.1.3 Bohr-Sommerfeld Quantization

A simple way to restrict the possible energy values of a harmonic oscillator is to specify a criterion, which selects specific classical trajectories in phase space. The Bohr-Sommerfeld quanitization rule consists in resctricting the area encircled by a certain motion. This quantity has the dimension of an action, or, the dimension of the Planck's constant h. The restriction, therefore, reads

$$\oint pdq = nh \tag{7.7}$$

The area equals the area of an ellipse with the axis

$$b = \sqrt{2mE} \qquad , \qquad a = \sqrt{\frac{2E}{m\omega^2}} \tag{7.8}$$

The area encircled by an ellipse is

$$\pi ab = \frac{2\pi E}{\omega} = nh \tag{7.9}$$

leading to the energy spectrum

$$E_n = \hbar\omega \tag{7.10}$$

7.2 Quantum Mechanical Harmonic Oscillator

In this section, we shall derive the energy spectrum of the harmonic oscillator from a solution of the Schrödinger equation:

$$i\hbar\dot{\Psi}(X,t) = [-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + \frac{m\omega^2}{2}q^2]\Psi(x,t) \tag{7.11}$$

7.2.1 Eigenvalue Problem: Hamilton Operator

A separation ansatz of the form

$$\Psi(x,t)=e^{-i\frac{E}{\hbar}t}\varphi(x) \tag{7.12}$$

leads us to the linear eigenvalue problem

$$E|\varphi>=[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2}+\frac{m\omega^2}{2}q^2]|\varphi> \tag{7.13}$$

which determines the energy spectrum and the corresponding eigenvectors.

For the following, it is convenient to introduce the dimensionless quantity

$$x=\sqrt{\frac{m\omega}{\hbar}}q \tag{7.14}$$

This transformation is taken in the form that the energy is measured in multiples of the quantity $\hbar\omega$.

The transformation turns the eigenvalue problem into

$$E\hbar\omega\varphi(x)=\epsilon\varphi(x)=\frac{1}{2}[-\frac{\partial^2}{\partial x^2}+x^2]\varphi(x) \tag{7.15}$$

where $E=\hbar\omega\epsilon$.

There are several methods to solve this eigenvalue problem. We shall first consider a method, which frequently is denoted as *Sommerfeld's polynom method* , which is based on a direct treatment of eq. (7.15) as an example of a so-called *Sturm-Liouville eigenvalue problem.* A second treatment will be based on an *algebraic method* using *occupation numbers.*

7.2.2 Hamilton Operator

As a first step towards the solution of the eigenvalue problem we consider the following representation of the Hamilton operator

$$\hat{H}=\frac{1}{2}[-\frac{\partial^2}{\partial x^2}+x^2] \tag{7.16}$$

We try to split the operator $[-\frac{\partial^2}{\partial x^2}+x^2]$ into a product of two operators. To this end we consider the product

$$[\frac{\partial}{\partial x}+x][-\frac{\partial}{\partial x}+x] \tag{7.17}$$

which would be a valid representation in the case that the opertors $\frac{\partial}{\partial x}$ and x would commute. We explicitly calculate

$$[-\frac{\partial}{\partial x}+x][\frac{\partial}{\partial x}+x]=-\frac{\partial^2}{\partial x^2}-[\frac{\partial}{\partial x},x]+x^2 \tag{7.18}$$

However, the commutator

$$[\frac{\partial}{\partial x},x]=1 \tag{7.19}$$

does not vanish. As a consequence,

$$\hat{H}=\frac{1}{2}[-\frac{\partial}{\partial x}+x][\frac{\partial}{\partial x}+x]+\frac{1}{2} \tag{7.20}$$

7.3 Sommerfeld's Polynom Method

7.3.1 Ground State

We can easily find a solution of the eigenvalue problem

$$\frac{1}{2}[-\frac{\partial}{\partial x}+x][\frac{\partial}{\partial x}+x]\varphi(x)=(\epsilon-\frac{1}{2})\varphi(x) \tag{7.21}$$

To this end, we seek a solution which obeys

$$[\frac{\partial}{\partial x}+x]\varphi_0(x)=0 \tag{7.22}$$

with the energy eigenvalue

$$\epsilon_0=\frac{1}{2} \tag{7.23}$$

The first order differential equation (7.22) is easily solved. It yields

$$\varphi_0(x)=Ne^{-\frac{x^2}{2}} \tag{7.24}$$

The normalization constant N is determined according to

$$1=N^2\int_{-\infty}^{\infty}dxe^{-x^2}=N^2\sqrt{\pi} \tag{7.25}$$

We can now summarize the expression for the so-called *ground state*

$$E=\frac{\hbar\omega}{2} \quad , \quad \varphi_0(x)=\frac{1}{\pi^{1/4}}e^{-\frac{x^2}{2}} \tag{7.26}$$

It will turn out that this state is the one with the lowest energy value, $E=\frac{\hbar\omega}{2}$.

7.3.2 Higher Eigenfunctions

In order to look for other eigenfunctions and eigenvalues we perform the ansatz

$$\varphi(x) = e^{-\frac{x^2}{2}} H(x) \qquad , \tag{7.27}$$

where $H(x)$ is a function which will be specified in the following.

To this end we calculate:

$$\frac{d^2}{dx^2}\varphi(x) = e^{-\frac{x^2}{2}} [\frac{d^2}{dx^2}H(x) + 2\frac{d}{dx}H(x)(-x) + x^2 H(x) - H(x) \tag{7.28}$$

The linear eigenvalue problem then reads:

$$\lambda H(x) = \frac{1}{2}(-\frac{d^2}{dx^2}H(x) + 2x\frac{d}{dx}H(x) + H(x)) \tag{7.29}$$

This is the so-called *Hermite eigenvalue problem.* Possible solutions are the so-called *Hermite polynomials.* It is an example of a so-called *Sturm-Liouville eigenvalue problem.*

It will turn out that we can find solutions only for special values of λ, provided the function $\varphi(x)$ is bounded. To this end, H(x) has to obey in the limit $|x| \to \infty$

$$|H(x)| < e^{\frac{x^2}{2}} \tag{7.30}$$

In this case $\varphi(x) \to 0$ at infinity, which is consistent with the interpretation as a probability density.

Let us consider various types of ansatz

a)

$$H_0 = c \qquad , \qquad \lambda = \frac{1}{2} \tag{7.31}$$

b)

$$H_1 = ax + b \tag{7.32}$$

We obtain

$$\lambda(ax + b) = \frac{1}{2}[2ax + ax + b] \tag{7.33}$$

The solvability condition reads

$$\lambda = \frac{3}{2} \qquad b = 0 \tag{7.34}$$

This suggests that we can look for an ansatz in terms of a polynomial: This is denoted as *Sommerfeld's method*:

$$H(x) = \sum_{k=0} x^k a_k \tag{7.35}$$

This yields

$$\begin{aligned}\lambda \sum_{k=0} a_k x^k &= \frac{1}{2}[-\sum_{k=2} a_k x^{k-2} k(k-1) + 2\sum_{k=1} a_k k x^k + \sum_{k=0} a_k x^k \\ &= \frac{1}{2}[-\sum_{k=0} a_{k+2} x^k (k+2)(k+1) + 2\sum_{k=1} a_k k x^k + \sum_{k=0} a_k x^k\end{aligned} \tag{7.36}$$

Now, we can read off the following recursion relation

$$a_{k+2} = \frac{[(2k+1) - 2\lambda]}{(k+2)(k+1)} a_k \tag{7.37}$$

We can distinguish solutions with even and odd parity. Solutions with *even parity* are obtained using $a_0 \neq 0, a_1 = 0$ $H(x) = H(-x)$, whereas solutions with *odd parity* $a_1 \neq 0, a_0 = 0$ $H(x) = -H(-x)$.

$$\lambda_n = n + \frac{1}{2} \tag{7.38}$$

The recursion relation yields for the even Hermite polynomials:

$$H^n_{k+2} = \frac{2(k-n)}{(k+1)(k+2)} H^n_k \qquad k = 0, 2, ..., n = 2l \tag{7.39}$$

The Taylor coefficients H^n_k for the odd Hermite polynomials obey the same recursion relation, however, with $k = 1, 3, ..n = 2l + 1$.

From this relation we see that the $H_n(x)$ are polynomials of degree n, since the solvability condition yields $a_n \neq 0$, $a_{n+2} = a_{n+4}... = 0$, and $a_{n+1} = a_{n+3}... = 0$. The functions $H_n(x)$ are even or odd polynomials in x, the so-called Hermite polynomials.

Even Hermite polynomials $H_n(x)$:

$n = 0$	1
$n = 2$	$4x^2 - 2$
$n = 4$	$16x^4 - 48x^2 + 12$

Odd Hermite polynomials $H_n(x)$:

$n = 1$	$2x$
$n = 3$	$8x^3 - 12x$
$n = 5$	$32x^5 - 160x^3 + 120x$

7.3.3 Properties of Hermite Polynomials

Orthogonality

The Hamilton-operator $\hat{H}$ is an Hermitian operator. As a consequence, the eigenfunctions $\varphi_n(x)$ form a complete orthogonal set. This implies the following relationship for the Hermite functions

$$< \varphi_n | \varphi_m >= \int_{-\infty}^{\infty} dx e^{-x^2} H_n(x) H_m(x) = 2^n n! \sqrt{\pi} \delta_{nm} \tag{7.40}$$

The normalization of the Hermite polynomials are introduced according to Abramowitz, Stegun, Handbook of Mathematical Functions.

Rodriques Formula

Hermite polynomials can be iteratively calculated by subsequent differentiation. We obtain

$$H_n(x) = e^{x^2} (x - \frac{d}{dx})^n e^{-x^2} \tag{7.41}$$

We shall give a proof of this relation below.

Generating Function

A generating function $G(x,t)$ is a function, whose Taylor expansion in t is related with a class of functions $f_n(x)$ according to

$$G(x,t) = \sum_{n=0} a_n f_n(x) t^n \tag{7.42}$$

The generating function for the Hermite polynomials is

$$G(x,t) = e^{2xt-t^2} = \sum_{n=0} \frac{1}{n!} H_n(x) t^n \tag{7.43}$$

Recurrence Relation

One can establish the following relation between the Hermite polynomial of orde n and $n+1$:

$$H_{n+1}(x) = 2x H_n(x) - \frac{\partial}{\partial x} H_n(x) \tag{7.44}$$

7.3.4 Spectrum and Eigenfunctions

We can now summarize: The energy spectrum of the harmonic oscillator is

$$E_n = \hbar\omega(n + \frac{1}{2}) \tag{7.45}$$

and the eigenfunctions are

$$\varphi_n(x) = \frac{1}{\sqrt{2^n n! \sqrt{\pi}}} e^{-\frac{x^2}{2}} H_n(x) \tag{7.46}$$

These eigenfunctions form a complete and orthogonal set.

$$\int_{-\infty}^{\infty} \varphi_n(x)\varphi_m(x) d\xi = N_n^2 \int_{-\infty}^{\infty} dx e^{-\xi^2} H_n(\xi) H_m(\xi) = \delta_{nm} \tag{7.47}$$

$$\sum_{n=0}^{\infty} \varphi_n(\xi)\varphi_m(\xi') = \sum_{n=0}^{\infty} N_n^2 e^{-\xi^2/2-\xi'^2/2} H_n(\xi) H_n(\xi') = \delta(x - x') \tag{7.48}$$

We can now express the eigenfunctions in terms of the coordinate $x = \sqrt{\frac{m\omega}{\hbar}} q$:

$$\varphi_n(q) = (\frac{m\omega}{\hbar})^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\sqrt{\frac{m\omega}{\hbar}} q) e^{-\frac{m\omega}{2\hbar} q^2} \tag{7.49}$$

7.4 Algebraic Treatment

7.4.1 Creation, Annihilation Operators

We start from the Hamilton operator

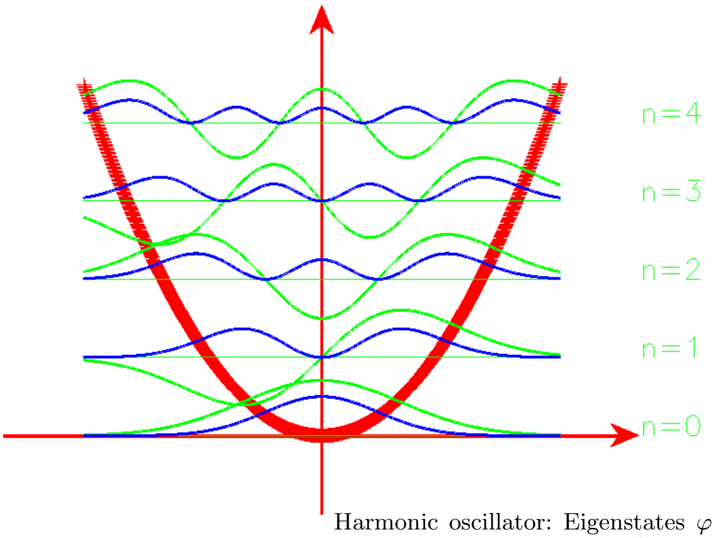
$$H = \hbar\omega \frac{1}{2}[-\frac{d^2}{dx^2} + x^2] \tag{7.50}$$

and introduce the operators b, b^* by the definitions

$$\begin{aligned} b &= \frac{1}{\sqrt{2}}[x + \frac{d}{dx}] \\ b^* &= \frac{1}{\sqrt{2}}[x - \frac{d}{dx}] \end{aligned} \tag{7.51}$$

It is straightforward to show that b^* is an operator adjoint to the operator b. To this end we consider

$$\begin{aligned} < \psi_1(x,t)|b|\psi_2(x,t) &= \sqrt{1}2 \int_{-\infty}^{\infty} dx \psi_1(x,t)^* (x + \frac{d}{dx}) \psi_2(x,t) \\ &= \sqrt{1}2 \int_{-\infty}^{\infty} dx [(x - \frac{d}{dx}) \psi_1(x,t)^*] \psi_2(x,t) \end{aligned} \tag{7.52}$$



Harmonic oscillator: Eigenstates $\varphi_n(x)$, and probability densities $|\varphi_n(x)|^2$.

We now express the Hamilton operator in terms of the operators $b^\dagger$, b. To this end we determine the operator product

$$
\begin{aligned}
b^*b &= \frac{1}{2}(x - \frac{d}{dx})(x + \frac{d}{dx}) = \frac{1}{2}[x^2 - \frac{d^2}{dx^2} - \frac{d}{dx}x + x\frac{d}{dx}] \\
&= \frac{1}{2}[x^2 - \frac{d^2}{dx^2} - 1] \qquad (7.53)
\end{aligned}
$$

This yields the explicit representation of the Hamilton operator in terms of the operators b^*, b:

$$H = \hbar\omega(b^*b + \frac{1}{2}) \qquad (7.54)$$

7.4.2 Commutators

In this subsection we determine various commutators, which will be needed in the algabraic treatment of the eigenvalue problem of harmonic oscillators.

First, we evaluate the commutator between b, $b^\dagger$:

$$
\begin{aligned}
[b, b^\dagger] &= \frac{1}{2}[(x + \frac{d}{dx})(x - \frac{d}{dx}) - (x - \frac{d}{dx})(x + \frac{d}{dx})] \\
&= \frac{1}{2}[2\frac{d}{dx}x - x\frac{d}{dx}] = 1 \qquad (7.55)
\end{aligned}
$$

This allows one to calculate in a straightforward manner the commutators $[b, b^\dagger b]$ and $[b^\dagger, b^\dagger b]$:

$$[b, b^\dagger b] = bb^\dagger b - b^\dagger bb = [b, b^\dagger]b = b \tag{7.56}$$

as well as

$$[b^\dagger, b^\dagger b] = b^\dagger b^\dagger b - b^\dagger bb^\dagger = b^\dagger[b^\dagger, b] = -b^\dagger \tag{7.57}$$

The commutators of the operators $b^\dagger$, b with the Hamilton operator H are

$$[b, H] = \hbar\omega b \tag{7.58}$$

$$[b^\dagger, H] = -\hbar\omega b^\dagger \tag{7.59}$$

7.4.3 The Ladder

We denote the eigenvectors of the Hamiltonian by $|n>$:

$$H|n>= E_n|n> \tag{7.60}$$

We observe the validity of the following property: If $|n>$ is an eigenstate of the Hamilton operator, then $Nb|n>$ is an eigenstate with energy $E_n - \hbar\omega$. The constant N is determined from the normalization of the eigenstate $|n>$:

$$< n|n >= 1 \tag{7.61}$$

For the proof we consider the relation

$$bH|n >= E_n b|n >= Hb|n > +\hbar\omega b|n > \tag{7.62}$$

where we have made use of the commutator $[b, H] = b$. We can rearrange this expression as follows

$$Hb|n >= (E_n - \hbar\omega)b|n > \tag{7.63}$$

From this relation we conclude that if $|n>$ is an eigenstate of the Hamilton operator, then $Nb|n>$ is an eigenstate with energy $E_n - \hbar\omega$. Therefore, the operator is denoted as an *annihilation operator* b.

We can make a similar statement concerning the operator $b^\dagger$. We start by calculating

$$b^* H|n >= E_n b^*|n >= Hb|n > -\hbar\omega b^*|n > \tag{7.64}$$

and rewrite this expression using the commutator as

$$Hb^*|n >= (E_n + \hbar\omega)b^*|n > \tag{7.65}$$

This indicates that $b^*|n>$ is an eigenstate with eigenvalue $E_n + \hbar\omega$. The operator $b^\dagger$ is denoted as *creation operator*.

7.4.4 Positivity of Energy Eigenstates

The expectation value of the Hamilton operator of the harmonic oscillator is positive:

Proof:

$$\begin{aligned} < \psi(x,t)|H|\psi(x,t) > &= \hbar\omega < \psi|b^{*}b + \frac{1}{2}|\psi > \\ &= \hbar\omega[< b\psi|b\psi > + \frac{1}{2}] \end{aligned} \tag{7.66}$$

As a consequence, there exist a *ground state*, i.e. the state with lowest energy eigenvalue. We denote this state by $|0>$. Inserting $|\psi >= |0>$ we obtain

$$\mathrm{e}_0 =< 0|b^{\dagger}b|0 > + \frac{1}{2} \geq \frac{1}{2} \tag{7.67}$$

Furthermore, since there is no eigenstate with $E < E_0$, we conclude on the basis of the relation

$$b|0 >= (E_0 - \hbar\omega)b|0 > \tag{7.68}$$

that

$$b|0 >= 0 \tag{7.69}$$

This fixes the energy eigenvalue of the ground state $|0>$ to

$$E_0 = \frac{1}{2}\hbar\omega \tag{7.70}$$

The eigenvalues of the excited state are obtained

$$\begin{aligned} E_1 &= \hbar\omega(1 + \frac{1}{2}) = E_0 + \hbar\omega \\ E_2 &= \hbar\omega(2 + \frac{1}{2}) = E_1 + \hbar\omega \\ E_3 &= \hbar\omega(3 + \frac{1}{2}) = E_2 + \hbar\omega \end{aligned} \tag{7.71}$$

It is straightforward to determine the ground state $|0>$ using the explicit definition of the operator b,

$$\frac{1}{\sqrt{2}}(x + \frac{d}{dx})\varphi_0(x) = 0 \tag{7.72}$$

We have already solved this differential equation of first order.

7.4.5 Occupation Number Operator

Thie operator $b^\dagger b$ has the meaning of an occupation number operator $\hat{n}$.

This becomes obvious from considering the eigenvalue problem

$$H|n>= \hbar\omega(b^\dagger b + \frac{1}{2})|n>= \left(n+\frac{1}{2}\right)\hbar\omega|n> \tag{7.73}$$

where we have explicitly inserted the obtained expressions for the energy eigenvalues E_n. This eigenvalue problem defines the eigenvalues and eigenvectors of the number operator $\hat{n}$

$$\hat{n}|n>= b^\dagger b|n>= n|n> \tag{7.74}$$

7.4.6 Normalization of Eigenstates

As we have seen above, we can determine the eigenvector $|n+1>$ from the knowledge of the eigenvector $|n>$:

$$|n+1>= Nb^*|n> \tag{7.75}$$

We now calculate the normalization constant N from the condition

$$\begin{aligned} < n+1|n+1> &= N^2 < b^*n|b^*n >= N^2 < n|bb^*|n> \\ &= N^2 < n|b^*b|n> +N^2 = N^2(n+1) < n|n> \end{aligned} \tag{7.76}$$

Since we assume $|n>$ to be normalized we explicitly obtain the relationship

$$|n+1>= \frac{1}{\sqrt{n+1}}b^*|n> \tag{7.77}$$

In a similar way we can determine the eigenstate $|n-1>$ from the knowlde of $|n>$:

$$|n-1>= Nb|n> \tag{7.78}$$

with the normalization constant to be determined from the condition

$$< n-1|n-1>= N^2 < bn|bn>= N^2 < n|b^*b|n>= N^2 < n|n>= 1 \tag{7.79}$$

Explicitly, we obtain

$$|n-1>= \frac{1}{\sqrt{n}}b|n> \tag{7.80}$$

Let us summarize:

$$\begin{aligned} |n+1> &= b^*\frac{1}{\sqrt{n+1}}|n> \\ |n-1> &= b\frac{1}{\sqrt{n}}|n> \end{aligned} \tag{7.81}$$

We can build each eigenvector starting from the ground state by a repeated iteration of (7.81):

$$|n>= \frac{1}{\sqrt{n!}}(b^*)^n|0> \tag{7.82}$$

Relation with Hermite's polynomials:

$$b|0>=\frac{1}{\sqrt{2}}(x+\frac{d}{dx})H_0(x)e^{-\frac{x^2}{2}}=0 \tag{7.83}$$

We obtain

$$|n>=H_n(x)e^{-\frac{x^2}{2}}=\frac{1}{\sqrt{n!}}\frac{1}{\sqrt{2}^n}(x-\frac{d}{dx})^nH_0e^{-\frac{x^2}{2}} \tag{7.84}$$

Which leads us to the following recursion relation for Hermite's polynomials:

$$H_n(x)=\frac{1}{\sqrt{n!}}\frac{1}{\sqrt{2}^n}e^{\frac{x^2}{2}}(x-\frac{d}{dx})^ne^{-\frac{x^2}{2}}H_0 \tag{7.85}$$

7.4.7 Uncertainty Relationships

We calculate the expectation of the variables q and p in the excited states. We obtain

$$\begin{aligned} q &= \sqrt{\frac{\hbar}{m\omega}}x=\sqrt{\frac{\hbar}{2m\omega}}(b+b^*) \\ p &= \frac{\hbar}{i}\frac{d}{dq}=\frac{\hbar}{i}\frac{d}{dq}=\frac{1}{i}\sqrt{\hbar m\omega}\frac{d}{dx} \\ &= \frac{1}{i}\sqrt{\frac{\hbar m\omega}{2}}(b-b^*) \end{aligned} \tag{7.86}$$

Let us now determine the expectation values

$$\begin{aligned} <n|q|n> &= \sqrt{\frac{\hbar}{2m\omega}}<n|(b+b^*)|n>=0 \\ <n|p|n> &= \frac{1}{i}\sqrt{\frac{\hbar m\omega}{2}}<n|(b-b^*)|n>=0 \end{aligned} \tag{7.87}$$

where we have exploited the fact that

$$<n|n-1>=0 \tag{7.88}$$

In order to determine the uncertainties we calculate

$$\begin{aligned} <n|q^2|n> &= \frac{\hbar}{2m\omega}<n|(b+b^*)^2|n> \\ &= \frac{\hbar}{2m\omega}<n|(b+b^*)^2|n>=\frac{\hbar}{m\omega}(n+\frac{1}{2}) \\ <n|p^2|n> &= -\frac{m\omega\hbar}{2}<n|(b-b^*)^2|n> \\ &= -\frac{m\omega\hbar}{2}<n|(b)^2-bb^*-b^*b+(b^*)^2|n> \\ &= m\omega\hbar(n+\frac{1}{2}) \end{aligned} \tag{7.89}$$

We can summarize the uncertainty relation as follows:

$$\sqrt{< n|q^2|n >< n|p^2|n >} = \hbar(n + \frac{1}{2}) \tag{7.90}$$

7.5 Coupled Harmonic Oscillators

7.5.1 Harmonic Oscillator in 3 Dimensions

In this subsection we consider the quantum mechanical description of the harmonic oscillator in three dimensions. The Hamilton operator reads

$$H(\mathbf{p}, \mathbf{q}) = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + \frac{m\omega^2}{2}[q_x^2 + q_y^2 + q_z^2] \tag{7.91}$$

This Hamilton operator can be written as the sum of three operators, each describing a one-dimensional harmonic oscillator:

$$H(\mathbf{p}, \mathbf{q}) = H_x(p_x, q_x) + H_y(p_y, q_y) + H_z(p_z, q_z) \tag{7.92}$$

In the following we use the Hamiltonian in the dimensionless variable $x = \sqrt{\frac{m\omega}{\hbar}}$, i.e.

$$H_x(p_x, x) = \hbar\omega\frac{1}{2}[-\frac{\partial^2}{\partial x^2} + x^2] \tag{7.93}$$

and, similarly, for the y,z directions.

We will show that the solution of the time independent Schrödinger equation

$$[H_x(p_x, x) + H_y(p_y, y) + H_z(p_z, z)]\varphi(x, y, z) = E\varphi(x, y, z) \tag{7.94}$$

can be reduced to the eigenvalue problem of the single harmonic oscillator.

To this end, we perform a *product ansatz* for the eigenfunction

$$\varphi(x, y, z) = \varphi_x(x)\varphi_y(y)\varphi_z(z) \tag{7.95}$$

Thereby, the functions $\varphi_x(x)$, $\varphi_y(y)$, $\varphi_z(z)$ are only functions of x, y, z, respectively. We insert this product ansatz into the eigenvalue problem (7.94) and consider the fact, that the operator $H_x(p_x, x)$ acts only on the function $\varphi(x)$:

$$H(p_x, x)\varphi_x(x)\varphi_y(y)\varphi_z(z) = \varphi_y(y)\varphi_z(z)H(p_x, x)\varphi_x(x) \tag{7.96}$$

and similar relations for $H_y(p_y, y)\varphi(x, y, z)$ and $H_z(p_z, z)\varphi(x, y, z)$. This property, which is based on the special form of the Hamiltonian (7.92), allows one to rewrite the eigenvalue problem (7.94) in the form

$$\frac{1}{\varphi_x(x)}H_x(p_x,x)\varphi_x(x)+\frac{1}{\varphi_y(y)}H_y(p_y,y)\varphi_y(y)+\frac{1}{\varphi_z(z)}H_z(p_z,z)\varphi_z(z)=E \tag{7.97}$$

From the fact that the left hand side is a sum of three functions, the first one depending on x, the second one on y and the third one on z, whereas the right hand side is independent on x, y, z we conclude that each term on the right hand side has to be a constant, which we denote as E^x, E^y, E^z:

$$\begin{aligned} H_x(p_x,x)\varphi_x(x) &= E^x\varphi_x(x)\\ H_x(p_y,y)\varphi_y(y) &= E^y\varphi_y(y)\\ H_z(p_z,z)\varphi_z(z) &= E^z\varphi_z(z) \end{aligned} \tag{7.98}$$

We recognize that, for each direction, we obtain the eigenvalue problem of the harmonic oscillator. Each energy eigenvalue E^x, E^y, E^z is then given by

$$\begin{aligned} E^x_{n_x} &= \hbar\omega[n_x+\frac{1}{2}]\\ E^y_{n_y} &= \hbar\omega[n_y+\frac{1}{2}]\\ E^z_{n_z} &= \hbar\omega[n_z+\frac{1}{2}] \end{aligned} \tag{7.99}$$

with $n_i = 0, 1, ...$ and the corresponding eigenfunctions

$$\varphi_{n_x}(x) = NH_{n_x}e^{-\frac{x^2}{2}} \tag{7.100}$$

As a consequence, the energy eigenvalues E of the Hamiltonian of the three dimensional harmonic oscillator are characterized by three quantum numbers n_x, n_y, n_z

$$\begin{aligned} E_{n_x,n_y,n_z} &= \hbar\omega[n_x+\frac{1}{2}]\\ &+\hbar\omega[n_y+\frac{1}{2}]+\hbar\omega[n_z+\frac{1}{2}] \end{aligned} \tag{7.101}$$

and the corresponding eigenfunction is the product of the eigenfunctions of the harmonic oscillators

$$\varphi_{n_x,n_y,n_z}(x,y,z) = \varphi_{n_x}(x)\varphi_{n_y}(y)\varphi_{n_z}(z) \tag{7.102}$$

For example, the ground state takes the form

$$\varphi_{0,0,0} = Ne^{-\frac{x^2+y^2+z^2}{2}} \tag{7.103}$$

These eigenfunctions form an orthornormal *product basis* of the Hilbert space of square integrable functions in R^3. Each wave function can be represented as a superposition of these basis functions

$$\Psi(x,y,z,t) = \sum_{n_x,n_y,n_z} c_{n_x,n_y,n_z}(t)\varphi_{n_x,n_y,n_z}(x,y,z) \tag{7.104}$$

and the expansion coefficients $c_{n_x,n_y,n_z}(t)$ can be determined from the function $\Psi(x,y,z,t)$ by the evaluation of the scalar products

$$c_{n_x,n_y,n_z}(t) = \int dx \int dy \int dz[\varphi_{n_x}(x)\varphi_{n_y}(y)\varphi_{n_z}(z)]^*\Psi(x,y,z,t) \tag{7.105}$$

We can reformulate the treatment of the three dimensional harmonic oscillator in terms of the occupation number formalism. To this end we introduce annihilation and generation operators for each direction. This allows one to rewrite the Hamiltonian (7.92) in the form

$$H = \hbar\omega_x[b_x^\dagger b_x + \frac{1}{2}] + \hbar\omega_y[b_y^\dagger b_y + \frac{1}{2}] + \hbar\omega_z[b_z^\dagger b_z + \frac{1}{2}] \tag{7.106}$$

Here, we have slightly generalized our treatment by considering different frequencies ω_x, ω_y, ω_z for each direction.

It is straightforward to formulate the commutators of the operators $b_i^\dagger$, b_i. The commutation rules can be summarized as follows

$$[b_i, b_j] = 0 \quad , \quad [b_i^\dagger, b_j^\dagger] = 0 \quad , \quad [b_i, b_j^\dagger] = \delta_{ij} \tag{7.107}$$

The eigenvectors of the Hamilton operator are

$$|n_x, n_y, n_z >= |n_x > |n_y > |n_z > \tag{7.108}$$

and obey

$$H|n_x, n_y, n_z >= E_{n_x,n_y,n_z}|n_x, n_y, n_z > \tag{7.109}$$

The occupation number operator acts on the eigenvectors in the following way

$$\hat{n}_x|n_x, n_y, n_z >= b_x^\dagger b_x|n_x, n_y, n_z >= n_x|n_x, n_y, n_z > \tag{7.110}$$

The eigenvectors can be determined from the ground state $|0,0,0>$ via the creation operators $b_i^\dagger$:

$$|n_x, n_y, n_z >= \frac{1}{\sqrt{n_x!}}\frac{1}{\sqrt{n_y!}}\frac{1}{\sqrt{n_z!}}(b_x^\dagger)^{n_x}(b_y^\dagger)^{n_y}(b_z^\dagger)^{n_z}|0,0,0> \tag{7.111}$$

7.5.2 Aplications: Molecular Oscillations

We consider a simple model of a molecule, which we describe by the momenta and the locations of its atoms. The atoms are glued together by electrons. We describe this binding force by an effective interacting between the atoms. This force is derived from the potential $V(|\mathbf{Q}_1, ..\mathbf{Q}_n)$. Newton's law yields

$$\frac{d}{dt}\mathbf{P}_i = -\nabla_{\mathbf{Q}_i} V(\mathbf{Q}_1, .., \mathbf{Q}_n) \tag{7.112}$$

A stable configuration of the molecule, denoted by $\mathbf{Q}_i^0$ is given by the condition

$$-\nabla_{\mathbf{Q}_i} V(\mathbf{Q}_1, .., \mathbf{Q}_n) = 0 \tag{7.113}$$

The Hamilton function is given by

$$H = \sum_i \frac{\mathbf{Q}_i^2}{2m_i} + V(\mathbf{Q}_1, .., \mathbf{Q}_n) \tag{7.114}$$

In order to describe oscillations of the molecule around the equilibrium state $\mathbf{Q}_i^0$ we introduce the deviations

$$\mathbf{Q}_i = \mathbf{Q}_i^0 + \mathbf{q}_i \qquad \mathbf{P}_i = \mathbf{p}_i \tag{7.115}$$

In terms of these quantities, the Hamilton function takes the form

$$H = \sum_j \frac{\mathbf{p_i}^2}{2m_i} + V(\mathbf{Q}_1^0 + \mathbf{q}_1, ..., \mathbf{Q}_n^0 + \mathbf{q}_n) \tag{7.116}$$

We can now expand the potential energy around the equilibrium positions and obtain

$$V(\mathbf{Q}_1^0 + \mathbf{q}_1, ..., \mathbf{Q}_n^0 + \mathbf{q}_n) = V(\mathbf{Q}_1^0, ..., \mathbf{Q}_n^0) + \frac{1}{2}\sum_{i,j} \nabla_{\mathbf{Q}_i^0} \nabla_{\mathbf{Q}_j^0} V(\mathbf{Q}_1^0, ..., \mathbf{Q}_n^0)\mathbf{q}_i\mathbf{q}_j \tag{7.117}$$

The first order term of the Taylor expansion vanishes, since we consider the equilibrium position.

We can lump all coordinates into the vectors $\mathbf{p}$ and $\mathbf{q}$ and obtain the Hamilton function in the harmonic approximation as

$$H = \sum_\alpha \frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}\sum_{\alpha,\beta} V_{\alpha,\beta} q_\alpha q_\beta \tag{7.118}$$

Furthermore, we perform the transformation

$$p'_\alpha = p_\alpha / \sqrt{\sqrt{m_\alpha}} \tag{7.119}$$

The Hamilton function then reads

$$H = \frac{\mathbf{p}^2}{2} + \frac{1}{2}\mathbf{q} \cdot V\mathbf{q} \tag{7.120}$$

We introduce the eigenvectors $\mathbf{u}^\alpha$ of the matrix V

$$V\mathbf{u}^\alpha = \lambda^\alpha \mathbf{u}^\alpha \tag{7.121}$$

and the transformation

$$\begin{aligned} \mathbf{q} &= \sum_\alpha c_\alpha(t)\mathbf{u}^\alpha \\ \mathbf{p} &= \sum_\alpha \dot{c}_\alpha(t)\mathbf{u}^\alpha \end{aligned} \tag{7.122}$$

As a result we obtain the Hamilton function

$$H = \sum_\alpha [|\dot{c}_\alpha| + \lambda^\alpha |c_\alpha|^2] \tag{7.123}$$

Since the equilibrium state is stable, all eigenvalues $\lambda^\alpha \geq 0$.

It turns out that due to translational invariance of the molecule there are at least three eigenvalues which are zero. The corresponding motions are related to a pure translation of the molecule.

8

Hydrogen Atom

8.1 Classical Model

The classical treatment of the Hydrogen atom consisting of a positive core surrounded by an electron is analogous to the Kepler problem of the motion of planets around the sun. The classical formulation of this problem is completely integrable.

Let us consider the mathematical formulation. The masses and the positions of the core and the electron are denoted by m_c, $\mathbf{r}_c$ and m_e, $\mathbf{r}_e$, respectively. Newton's law reads

$$\begin{aligned} m_e\ddot{\mathbf{r}}_e &= \mathbf{K}(\mathbf{r}_e - \mathbf{r}_c) \\ m_c\ddot{\mathbf{r}}_c &= -\mathbf{K}(\mathbf{r}_e - \mathbf{r}_c) \end{aligned} \tag{8.1}$$

where we have denoted the force between core and electron by $\mathbf{K}(\mathbf{r})$.

The Hamilton function reads

$$H = \frac{\mathbf{p}_e^2}{2m_e} + \frac{\mathbf{p}_c^2}{2m_c} + V(|\mathbf{r}_e - \mathbf{r}_c|) \tag{8.2}$$

8.1.1 Center of Mass, Relative Motion

As is well-known, the classical two body problem can be separated into the motion of the center of mass, $\mathbf{R} = \frac{m_e\mathbf{r}_e + m_c\mathbf{r}_c}{m_e+m_c}$, and the relative coordinate $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_c$:

$$\begin{aligned} \ddot{\mathbf{R}} &= 0 \\ m\ddot{\mathbf{r}} &= \mathbf{K}(\mathbf{r}) \end{aligned} \tag{8.3}$$

m denotes the reduced mass defined according to

$$m = \frac{m_e m_c}{m_e + m_c} \tag{8.4}$$

The motion of the center of mass and the relative motion decouple.

The Hamilton function of the relative motion reads

$$H = \frac{\mathbf{p}^2}{2\mu} + V(r) \tag{8.5}$$

$\mathbf{r}$ is the relative coordinate. The potential for the case of the Hydrogen atom is given by

$$V = -\frac{\gamma}{r} = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r} \tag{8.6}$$

8.1.2 Conservation Laws

The classical problem (Kepler problem) is integrable due to the existence of the conservation of energy and angular momentum.

8.2 Quantization

$$H = -\frac{\hbar^2}{2m_c}\Delta_{r_c} - \frac{\hbar^2}{2m_e}\Delta_{r_e} + V(|\mathbf{r}_e - \mathbf{r}_c|) \tag{8.7}$$

We introduce relative coordinate and center of mass coordinate according to

$$\begin{aligned} \mathbf{r} &= \mathbf{r}_e - \mathbf{r}_c \\ \mathbf{R} &= \frac{m_e\mathbf{r}_e + m_c\mathbf{r}_c}{m_e + m_c} \end{aligned} \tag{8.8}$$

The inverse transform is given by $(M = m_e + m_c)$

$$\begin{aligned} \mathbf{r}_e &= \mathbf{R} + \frac{m_c}{M}\mathbf{r} \\ \mathbf{r}_c &= \mathbf{R} + \frac{m_e}{M}\mathbf{r} \end{aligned} \tag{8.9}$$

This transformation yields the Hamiltonian

$$H = -\frac{\hbar^2}{2M}\Delta_R - \frac{\hbar^2}{2m}\Delta_r + V(|\mathbf{r}|) \tag{8.10}$$

The proof is straightforward. We express the gradients with respect to $\mathbf{r}_e$ and $\mathbf{r}_c$ in terms of $\mathbf{R}$ and $\mathbf{r}$:

$$\begin{aligned} \nabla_{\mathbf{r}_e} &= \frac{m_e}{M}\nabla_R + \nabla_r \\ \nabla_{\mathbf{r}_c} &= \frac{m_c}{M}\nabla_R - \nabla_r \end{aligned} \tag{8.11}$$

Subsequently, we calculate

8.2.1 Separation of Relative and Center of Mass Motion

The Hamiltonian of the joint motion of core and electron is separated into the Hamiltonian for the center of mass, H_R, and the Hamiltonian H_r of the relative motion:

$$H = H_R + H_r \tag{8.12}$$

The center of mass part, H_R, is the Hamiltonian of the motion of a free particle.

For the solution of the time dependent Schrödinger equation we can perform a separation ansatz

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \Psi_R(\mathbf{R}, t)\Psi_r(\mathbf{r}, t) \tag{8.13}$$

This separation ansatz yields the two Schrödinger equations

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\Psi_R(\mathbf{R}, t) &= H_R\Psi_R(\mathbf{R}, t) \\ i\hbar\frac{\partial}{\partial t}\Psi_r(\mathbf{r}, t) &= H_r\Psi_r(\mathbf{r}, t) \end{aligned} \tag{8.14}$$

8.2.2 Time Independent Schrödinger Equation

The ansatz

$$\Psi_r(\mathbf{r}, t) = e^{-i\frac{E}{\hbar}t}\psi(\mathbf{r}) \tag{8.15}$$

leads to the time independent Schrödinger equation

$$E\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r}) + V(|\mathbf{r}|)\psi(\mathbf{r}) \tag{8.16}$$

8.3 Hamilton Operator in Spherical Coordinates

In this section we consider the quantum mechanical treatment of the motion of a particle of mass m in a central force field, which is obtained from the potential

$$\mathbf{K}(\mathbf{r}) = -\nabla_r V(r) = -\mathbf{e}_r V'(r) \tag{8.17}$$

Due to spherical symmetry, it is convenient to express the wave function $\Psi(\mathbf{r}, t)$ in spherical coordinates r, θ, φ:

$$\begin{aligned} x &= rsin\theta cos\varphi \\ y &= rsin\theta sin\varphi \\ z &= rcos\theta \end{aligned} \tag{8.18}$$

Our first task consists in expressing the operators ∇, Δ in spherical coordinates.

8.3.1 Gradient and Momentum Operator: Spherical Coordinates

In this subsection, we shall derive a representation of the nabla operator, and, in turn, the momentum operator in spherical coordinates. Our starting point is the decomposition of the gradient of a function $f(\mathbf{r})$ into a radial and a transversal part:

$$\nabla f = \mathbf{e}_r \mathbf{e}_r \cdot (\nabla f) - \mathbf{e}_r \times [\mathbf{e}_r \times (\nabla f)] \tag{8.19}$$

where $\mathbf{e}_r$ denotes the unit vector in radial direction:

$$[\mathbf{e}_r]_i = \frac{r_i}{r} \tag{8.20}$$

It is straightforward to proof that in spherical coordinates

$$\mathbf{e}_r \cdot \nabla = \frac{r_j}{r} \frac{\partial}{\partial r_j} = \frac{\partial}{\partial r} \tag{8.21}$$

We consider now the momentum operator

$$\begin{aligned} \mathbf{p} &= \frac{\hbar}{i} \nabla \\ &= \mathbf{e}_r p_r - \frac{1}{r} \mathbf{e}_r \times \mathbf{L} \end{aligned} \tag{8.22}$$

Here, we have defined the *operator of angluar momentum*:

$$\mathbf{L} = \mathbf{r} \times \frac{\hbar}{i} \nabla \tag{8.23}$$

We can now determine the Laplacian in terms of the operator of angular momentum. We calaculate

$$\begin{aligned} \frac{\partial}{\partial r_i} \frac{\partial}{\partial r_i} &= \frac{\partial}{\partial r_i} [\frac{r_i}{r} \frac{\partial}{\partial r} - \epsilon_{ijk} \frac{r_j}{r} \frac{i}{\hbar} L_k] \\ &= \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} - \frac{i}{\hbar} \epsilon_{ijk} \left[\left(\frac{\partial}{\partial r_i} \frac{r_j}{r} \right) + \frac{r_j}{r} \frac{\partial}{\partial r_i} L_k \right] \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{i}{\hbar} \epsilon_{ijk} \frac{r_j}{r} \frac{\partial}{\partial r_i} L_k \end{aligned} \tag{8.24}$$

We can summarize the representation of the Laplacian in terms of the operator of angular momentum

$$\Delta = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{1}{r^2 \hbar^2} \mathbf{L}^2 \tag{8.25}$$

In the appendix we shall explicitly specify this operator in spherical coordinates:

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}] \tag{8.26}$$

As a consequence, the Hamiltonian for the motion of a particle in a spherically symmetric potential reads

$$H = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\mathbf{L}^2}{2mr^2} + V(r) \tag{8.27}$$

Thereby, we have defined the operator

$$\mathbf{L}^2 = -\hbar^2[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}] \tag{8.28}$$

As we shall see this operator is related to the operator of angular momentum, $\mathbf{L}$

8.3.2 Separation Ansatz

The time independent Schrödinger equation

$$H\psi(\mathbf{x}) = E\psi(\mathbf{x}) \tag{8.29}$$

is a partial differential equation. It is straightforward to perform the following separation ansatz

$$\psi(\mathbf{x}) = R(r)Y(\Theta,\varphi) \tag{8.30}$$

Thereby, we exploit the fact that $\mathbf{L}^2$ is an operator acting only on the function $Y(\Theta,\varphi)$. Inserting this ansatz into time independent Schrödinger equation we obtain

$$E = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \frac{1}{2mr^2}\frac{\mathbf{L}^2Y(\theta,\varphi)}{Y(\theta,\varphi)} \tag{8.31}$$

In order that this separation ansatz makes sense, the quantity

$$\frac{\mathbf{L}^2Y(\theta,\varphi)}{Y(\theta,\varphi)} = \hbar^2\Omega \tag{8.32}$$

has to be a constant, which we take to be $\hbar^2\Omega$. We recognize that this condition leads to an eigenvalue problem corresponding to the operator $\mathbf{L}^2$:

$$\mathbf{L}^2Y(\theta,\varphi) = \hbar^2\Omega Y(\theta,\varphi) \tag{8.33}$$

The investigation of this eigenvalue problem will be performed in the next section.

The separation ansatz leads us to the following eigenvalue problem for the radial part $R(r)$ of the wave function

$$[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hbar^2\Omega}{2mr^2} + V(r)]R(r) = ER(r) \tag{8.34}$$

The eigenvalue problem for the motion of a particle in a central potential is decomposed into two eigenvalue problems, one for the angular part, the other for the radial part of the wave function.

8.4 Angular Momentum

8.4.1 Eigenvalue Problem

In this subsection we discuss a direct solution of the eigenvalue problem

$$\mathbf{L}^2 Y(\theta,\varphi) = \hbar^2 \Omega Y(\theta,\varphi) \tag{8.35}$$

with the explicit form of the operator $\mathbf{L}^2$ in spherical coordinates:

$$-[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}]Y(\theta,\varphi) = \Omega Y(\theta,\varphi) \tag{8.36}$$

We perform the ansatz

$$Y(\theta,\varphi) = Y_m(\theta)e^{im\varphi} \tag{8.37}$$

In order to fullfill the boundary condition

$$Y(\theta,\varphi+2\pi) = Y(\theta,\varphi) \tag{8.38}$$

we have to assume that $m = 0, \pm 1, ...$ This yields the following equation

$$-[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta} - \frac{m^2}{sin^2\theta}]Y_m(\theta) = \Omega Y_m(\theta) \tag{8.39}$$

We furthermore introduce the coordinate

$$x = cos\theta \qquad \frac{d}{d\theta} = \frac{dx}{d\theta}\frac{d}{dx} = -\sin\theta\frac{d}{dx} \tag{8.40}$$

to obtain the equation

$$\frac{d}{dx}(1-x^2)\frac{d}{dx}P_l^m - \frac{m^2}{1-x^2}P_l^m(x) = -\Omega P_l^m(x) \tag{8.41}$$

This is the *associated Legendre differential equation.*

In the case $m = 0$ we obtain the *Legendre differential equation*, which can be written in the form

$$(1-x^2)P_l''(x) - 2xP_l'(x) = \lambda P_l(x) \tag{8.42}$$

The associated Legendre functions are obtained from the Legendre functions by differentiation with respect to x:

$$P_l^m(x) = (-1)^m(1-x^2)^{m/2}\frac{d^m}{dx^m}P_l(x) \tag{8.43}$$

l	$P_l(x)$
0	1
1	x
2	$\frac{1}{2}(3x^2-1)$
3	$\frac{1}{2}(5x^3-3x)$
4	$\frac{1}{8}(35x^4-30x^2+3)$

Legendre Polynomials

Sommerfeld's Polynomial Ansatz

In the following we use Sommerfelds polynom ansatz in order to solve the eigenvalue problem

$$(1-x^2)P'' - 2xP' = \lambda P \tag{8.44}$$

We look for a solution in terms of the Taylor expansion of $P(x)$ at $x = 0$.

$$P(x) = \sum_{k=0} a_k x^k \tag{8.45}$$

This expansion should converge in the interval $-1 \leq x \leq 1$.

Inserting the Taylor expansion into the eigenvalue proble yields

$$\sum_{k=0} a_k k(k-1)(x^{k-2} - x^k) - 2ka_k x^k = \sum_{k=0} \lambda a_k x^k \tag{8.46}$$

so that we obtain the recursion relation

$$a_{k+2}(k+1)(k+2) - a_k(2k + k(k-1) + \lambda) = 0 \tag{8.47}$$

This recursion relation can be cast into the form

$$a_{k+2} = \frac{(k(k+1) - \lambda)}{(k+1)(k+2)} a_k \tag{8.48}$$

Polynomial solutions exist provided the Taylor expansion terminates at $k = l$. This condition immediately yields the eigenvalues:

$$\lambda_l = -l(l+1) \tag{8.49}$$

The corresponding polynomial eigenfunctions are obtained by the recursion relation.

Rodrigues Formula

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l \tag{8.50}$$

Generating Function

$$\frac{1}{\sqrt{1 - 2xt + t^2}} = \sum_{l=0} t^l P_l(x) \tag{8.51}$$

Bonnet's Recursion Relation

$$(l+1)P_{l+1}(x) = (2l+1)xP_l(x) - lP_{l-1}(x) \tag{8.52}$$

Orthogonality Property

$$\int_{-1}^{1} dx P_l(x) P_{l'}(x) = \delta_{l,l'} \frac{2}{2l+1} \tag{8.53}$$

Parity:

$$P_l(x) = (-1)^l P_l(-x) \tag{8.54}$$

8.4.2 Algebraic Treatment

The operator of angular momentum is defined by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times \frac{\hbar}{i}\nabla \tag{8.55}$$

or, explicitly

$$L_i = \frac{\hbar}{i}\epsilon_{ijk} r_j \frac{\partial}{\partial r_k} \tag{8.56}$$

In cartesian ccordinates the x,y,z- components of the operator reads

$$L_x = \frac{\hbar}{i}[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}] L_z = \frac{\hbar}{i}[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}] L_z = \frac{\hbar}{i}[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}] \tag{8.57}$$

As shown in the appendix, the operators of angular momentum expressed in spherical coordinates are as follows:

$$\begin{aligned} L_x &= \frac{\hbar}{i}[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}] \\ &= -\frac{\hbar}{i}[sin\varphi\frac{\partial}{\partial\theta} + cot\theta cos\varphi\frac{\partial}{\partial\varphi}] \\ L_y &= \frac{\hbar}{i}[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}] \\ &= \frac{\hbar}{i}[cos\varphi\frac{\partial}{\partial\theta} - cot\theta sin\varphi\frac{\partial}{\partial\varphi}] \\ L_z &= \frac{\hbar}{i}[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}] \\ &= \frac{\hbar}{i}\frac{\partial}{\partial\varphi} \end{aligned} \tag{8.58}$$

Using these representations we can determine $\mathbf{L}^2$:

$$\mathbf{L}^2 = -\hbar^2\{\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\} \tag{8.59}$$

8.4.3 Eigenvalue Problem connected with $\mathbf{L}^2$, L_z

We investigate the eigenvalue problems

$$\begin{aligned} L^2 Y(\theta,\varphi) &= \hbar^2 \Omega Y(\theta,\varphi) \\ L_z Y(\theta,\varphi) &= \hbar m \Omega Y(\theta,\varphi) \end{aligned} \tag{8.60}$$

Our treatment will be algebraic.

8.4.4 Commutation relations

The various components of the operator of angular momentum do not commute. The following commutation rules follow from the definition of the operator of angular momentum:

$$L_i L_j - L_j L_i = \epsilon_{ijk} i\hbar L_k \tag{8.61}$$

Proof:

$$\begin{aligned} L_i L_j &= -\hbar^2 \{\epsilon_{ikl}\epsilon_{jmn} x_k \frac{\partial}{\partial x_l} x_m \frac{\partial}{\partial x_n}\} \\ &= -\hbar^2 \{\epsilon_{ikl}\epsilon_{jmn} x_k x_m \frac{\partial}{\partial x_l}\frac{\partial}{\partial x_n}\} \\ &\quad - \hbar^2 \{\epsilon_{ikl}\epsilon_{jmn}\delta_{lm} x_k \frac{\partial}{\partial x_n}\} \end{aligned} \tag{8.62}$$

leading to the commutator We interchange the indices i and j and obtain for the commutator

$$[L_i, L_j] = -\hbar^2 \{\epsilon_{ikl}\epsilon_{jmn}\delta_{lm} x_k \frac{\partial}{\partial x_n}\} + \hbar^2 \{\epsilon_{jkl}\epsilon_{imn}\delta_{lm} x_k \frac{\partial}{\partial x_n}\} \tag{8.63}$$

With the help of

$$\epsilon_{ikl}\epsilon_{ljn} = \delta_{ij}\delta_{kn} - \delta_{in}\delta_{jk} \tag{8.64}$$

we end up with the commutators

$$[L_i, L_j] = -\hbar^2 [x_j \frac{\partial}{\partial x_i} - x_i \frac{\partial}{\partial x_j}] = i\hbar \epsilon_{ijk} L_k \tag{8.65}$$

The operators L_i are generators of the Lie-group SO(3).

The Operator $\mathbf{L}^2$

We define tha operator $\mathbf{L}^2$

$$\mathbf{L}^2 = \sum_i L_i^2 = L_1^2 + L_2^2 + L_3^2 \tag{8.66}$$

It is straightforward to determine the commutators between the components of $\mathbf{L}$ and $\mathbf{L}^2$:

$$[L_i, \mathbf{L}^2] = L_i \sum_k L_k^2 - \sum_k L_k^2 L_i \tag{8.67}$$

We calculate the commutator between

$$\begin{aligned}[L_i, L_k^2] &= L_i L_k^2 - L_k^2 L_i = +L_k L_i L_k + [L_i, L_k] L_k - L_k^2 L_i \\ &= L_k^2 L_i + L_k [L_k, L_i] + [L_i, L_k] L_k - L_k^2 L_i = \\ &= i\hbar \sum_j [L_k \epsilon_{kij} L_j - \epsilon_{kij} L_j L_k] = i\hbar \sum_j \epsilon_{kij} [L_k L_j - L_j L_k]\end{aligned} \tag{8.68}$$

If we sum over k, we obtain

$$[L_i, \mathbf{L}^2] = 0 \tag{8.69}$$

Ladder Operators

It is convenient to define the operators

$$\begin{aligned}L_+ &= L_x + iL_y \\ L_- &= L_x - iL_y = (L_+)^\dagger\end{aligned} \tag{8.70}$$

They will play a similar role as the operators $b^\dagger$ and b for the harmonic oscillator.

The Eigenvalue Problem

We consider the eigenvalue problems

$$\begin{aligned}\mathbf{L}^2 |lm> &= \hbar^2 \Omega |lm> \\ L_z |lm> &= \hbar m |lm>\end{aligned} \tag{8.71}$$

Thereby, we have denoted the eigenvectors by $|lm>$. We need to indices to enumerate the eigenvectors since they are eigenvectors to the operators $L - z$ and $\mathbf{L}^2$.

a) We first proof the following inequality between the eigenvalues $m\hbar$ and $\Omega\hbar$:

$$\Omega \geq m^2 \tag{8.72}$$

For the proof we explicitly consider

$$[L_x^2 + L_y^2 + L_z^2]|lm >= [L_x^2 + L_y^2 + m^2\hbar^2]|lm >= \hbar^2 \Omega |lm > \tag{8.73}$$

which leads us to

$$[L_x^2 + L_y^2]|lm >= \hbar^2(\Omega - m^2)|lm > \tag{8.74}$$

L_x, L_y are hermitian operators such that

$$< lm|L_x^2 + L_y^2|lm >=< L_x lm|L_x lm > + < L_x lm|L_x lm >\geq 0 \tag{8.75}$$

As a result, we obtain the inequality

$$(\Omega - m^2) \geq 0 \tag{8.76}$$

b) We now show that L_+ and L_- are ladder operators: Provided that $|lm >$ is an eigenfunction of $\mathbf{L}^2$ and L_z with eigenvalue $m\hbar$, $L_\pm|lm >$ is an eigenfunction of $\mathbf{L}^2$ and L_z with eigenvalue $(m \pm 1)\hbar$

Proof: The operators $L_\pm$ commute with the operator $\mathbf{L}^2$. Therefore, they possess common eigenvectors. It remains to show that $L_\pm|lm >$ is also an eigenfunction of L_z. To this end we calculate the commutator

$$[L_z, L_\pm] = [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm \hbar L_x = \pm\hbar L_\pm \tag{8.77}$$

The proof is straightforward:

$$L_\pm L_z Y_{lm} = -[L_z, L_\pm]Y_{lm} + L_z L_\pm Y_{lm} = \hbar m L_\pm Y_{lm} \tag{8.78}$$

Using the commutator (8.77) we conclude

$$L_z L_\pm Y_{lm} = \hbar(m \pm 1)Y_{lm} \tag{8.79}$$

so that up to a normalization constant N_{lm}

$$L_\pm Y_{lm} = N_{lm} Y_{l,m\pm1} \tag{8.80}$$

c) We are now in the position to determine the possible eigenvalues Ω and m. Since the quantity

$$\Omega - m^2 \geq 0 \tag{8.81}$$

there exist minimal and maximal values m_{min}, m_{max}. Since the operators $L_\pm$ are ladder operators we conclude that

$$L_- Y_{lm_{min}} = 0 \qquad , \qquad L_+ Y_{lm_{max}} = 0 \tag{8.82}$$

We now determine the eigenvalues of $\mathbf{L}^2$. To this end we consider

$$L_- L_+ = (L_x - iL_y)(L_x + iL_y) = L_x^2 + L_y^2 + i\hbar[L_x, L_y] \tag{8.83}$$

$$L_-L_+ = L_x^2 + L_y^2 - \hbar L_z = \mathbf{L}^2 - L_z(L_z + \hbar) \tag{8.84}$$

In an analogous way, we obtain

$$L_+L_- = L_x^2 + L_y^2 + \hbar L_z = \mathbf{L}^2 - L_z(L_z - \hbar) \tag{8.85}$$

Thus,

$$L_-L_+|lm_{max}>= 0 = \hbar^2(\Omega - m_{max}^2 - m_{max})|lm_{max}> \tag{8.86}$$

$$L_+L_-|lm_{min}>= 0 = \hbar^2(\Omega - m_{min}^2 + m_{min})|lm_{min}> \tag{8.87}$$

However, we have to postulate that

$$\Omega = m_{max}(m_{max} + 1) = m_{min}(m_{min} - 1) \tag{8.88}$$

This relation can be combined to yield

$$\begin{aligned} 0 &= m_{max}(m_{max} + 1) - m_{min}(m_{min} - 1) \\ &= (m_{max} + m_{min})(m_{max} - m_{min} + 1) \end{aligned} \tag{8.89}$$

From here, we conclude

$$m_{max} = -m_{min} \tag{8.90}$$

Possibilities: $m_{min} = -l$

Angular momentum: $m = -l, .., 0, .., l$

Spin $l = 1/2$, $l = \frac{3}{2}$, $l = \frac{5}{2}$

d) The Ladder

We specify explicitly the relations between the eigenfunctions $lm >$ and $l, m \pm 1 >$ which arise due to the operators $L_\pm$. We have the relation

$$L_\pm|l, m >= N_{l,\pm}|l, m \pm 1 > \tag{8.91}$$

We now determine the normalization constant $N_{l,\pm}$. We obtain

$$\begin{aligned} < l, m \pm 1|l, m \pm 1 > &= \frac{1}{N_{l,\pm}^2} < L_\pm lm|L_\pm lm > \\ &= \frac{1}{N_{l,\pm}^2} < lm|L_\mp L_\pm|lm > \end{aligned} \tag{8.92}$$

We can now express the operators $L_\mp L_\pm$ in terms of $\mathbf{L}^2$, L_z:

$$L_\mp L_\pm = \mathbf{L}^2 - L_z(L_z \pm \hbar) \tag{8.93}$$

Therefore,

$$N_{l,\pm} = \hbar\sqrt{l(l+1) - m(m \pm 1)} \tag{8.94}$$

We are now in a position to summarize the relations induced by the ladder operator:

$$\begin{aligned} L_+|l, m > &= \hbar\sqrt{l(l+1) - m(m+1)}|l, m+1 > \\ L_-|l, m > &= \hbar\sqrt{l(l+1) - m(m-1)}|l, m-1 > \end{aligned} \tag{8.95}$$

These relations especially include

$$L_-|l, -l >= 0 \qquad L_+|l, l >= 0 \tag{8.96}$$

Spherical Harmonics

The operators $L_\pm$ can be represented in spherical coordinates

$$L_\pm = \hbar e^{i\pm\varphi}[\pm\frac{\partial}{\partial\theta} + icot\theta\frac{\partial}{\partial\varphi}] \tag{8.97}$$

We can successively obtain the spherical harmonics starting with $Y_{l,-l}$. To this end we notice that

$$L_- Y_{l,-l} = \hbar e^{i\pm(1-l)\varphi}[-\frac{\partial}{\partial\theta} + lcot\theta]Y_{l,-l} = 0 \tag{8.98}$$

This is a first order differential equation which can be solved in a straightforward manner:

$$Y_{l,-l} = N_l sin^l \Theta e^{-il\varphi} \tag{8.99}$$

The normalization constant is determined by the relationship

$$\int sin\theta d\theta d\varphi N_l^2 sin^{2l}\Theta = 2\pi N_l^2 \int sin\theta d\theta sin^{2l}\Theta \tag{8.100}$$

The eigenvectors $Y_{l,m}$ can be determined in a straightforward way using the ladder operator $L_\pm$:

$$Y_{l,m+1} = \frac{1}{\hbar}\frac{1}{\sqrt{l(l+1) - m(m+1)}}L_+ Y_{l,m} \tag{8.101}$$

In a similar way, we obtain the relationship

$$Y_{l,m-1} = \frac{1}{\hbar}\frac{1}{\sqrt{l(l+1) - m(m-1)}}L_- Y_{l,m} \tag{8.102}$$

Spherical Harmonics for Small l

a) $l = 0$ (s-Orbital)

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \tag{8.103}$$

b) $l = 1$ (p-Orbital)

$$Y_{l,0} = \sqrt{\frac{3}{4\pi}}cos\theta = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \tag{8.104}$$

$$Y_{l,\pm 1} = \sqrt{\frac{3}{8\pi}}sin\theta e^{i\pm\varphi} = \sqrt{\frac{3}{8\pi}}\frac{x \pm iy}{r} \tag{8.105}$$

c) $l = 2$ (d-Orbital)

$$Y_{2,0} = \sqrt{\frac{5}{16\pi}}(3cos^2\theta - 1) \tag{8.106}$$

$$Y_{2,1} = \sqrt{\frac{15}{8\pi}}3sin\theta cos\theta e^{i\varphi} \tag{8.107}$$

$$Y_{2,2} = \sqrt{\frac{15}{32\pi}}sin^2\theta e^{2i\varphi} \tag{8.108}$$

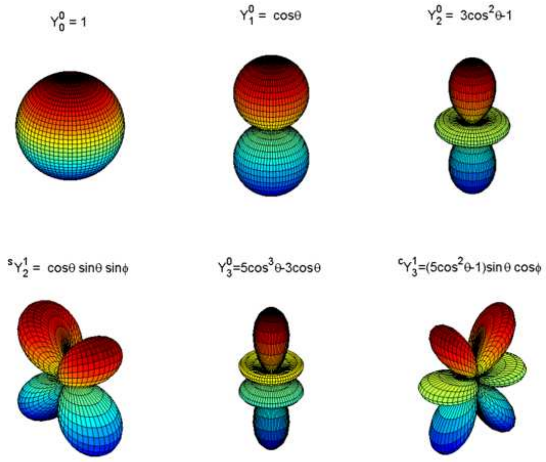


Fig. 8.1. Visualization of low order spherical harmonics

8.5 Radial Eigenfunctions: Hydrogen Atom

We adress the eigenvalue problem determining the radial part of the wave function of the Hydrogen atom.

$$\{-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{\gamma}{r}\}\psi(r) = E\psi(r) \tag{8.109}$$

We perform the ansatz

$$\psi(r) = \frac{u(r)}{r} \tag{8.110}$$

since

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\frac{u(r)}{r} = \frac{1}{r}\frac{\partial}{\partial r}\frac{\partial}{\partial r}ru(r) \tag{8.111}$$

Furthermore, we introduce a dimensionless radius ρ, where a is Bohr's radius,

$$\rho = \frac{r}{a} \tag{8.112}$$

and obtain

$$\{-\frac{\hbar^2}{2\mu a^2}\frac{\partial}{\partial\rho}\frac{\partial}{\partial\rho}u(\rho) + \frac{\hbar^2 l(l+1)}{2\mu a^2} - \frac{\gamma}{\rho a}\}u(\rho) = Eu(\rho) \tag{8.113}$$

$$\{-\frac{\partial^2}{\partial\rho^2}u(\rho) + \frac{l(l+1)}{2\rho^2} - \frac{2}{\rho}\}u(\rho) = \epsilon u(\rho) \tag{8.114}$$

Thereby, we have introduced a dimensionless quantity ϵ related with the energy

$$\begin{aligned}\epsilon &= \frac{E}{R_H}\\ R_H &= \frac{\mu\gamma^2}{2\hbar^2}\\ a &= \frac{\hbar^2}{\mu\gamma}\end{aligned} \tag{8.115}$$

a: Bohr's radius, R_H Rydberg constant

8.5.1 Asymptotic behaviour $\rho \to \infty$

The asymptotic behaviour for $\rho \to \infty$ is obtained from (8.114):

$$\frac{d^2}{d\rho^2}u = -\epsilon u \tag{8.116}$$

We are interested in bound states: $\epsilon < 0$. The solution of (8.116) is the function

$$u(\rho) = ae^{\sqrt{|\epsilon|}\rho} + be^{-\sqrt{|\epsilon|}\rho} \tag{8.117}$$

The function $u(\rho)$ should approach 0 for large values of ρ. This results in $a = 0$.

8.5.2 Sommerfeld's Method

We determine the radial functions $u(\rho)$ by Sommerfeld's method. To this end we perform the ansatz

$$u(\rho) = e^{-\alpha\rho}P(\rho) \tag{8.118}$$

with

$$\alpha = \sqrt{-\epsilon} \tag{8.119}$$

and obtain the following differential equation defining the function $P(\rho)$:

$$\{\frac{\partial^2}{\partial\rho^2} - 2\alpha\frac{\partial}{\partial\rho} - \frac{l(l+1)}{2\rho^2} + \frac{2}{\rho}\}P(\rho) = 0 \tag{8.120}$$

This differential equation defines an eigenvalue problem.

The asymptotic behaviour for small values of ρ is determined from

$$\{\frac{\partial^2}{\partial\rho^2} - \frac{l(l+1)}{2\rho^2}\}P(\rho) = 0 \tag{8.121}$$

This yields the solution

$$P(\rho) = c\rho^{(l+1)} + d\rho^{-l} \tag{8.122}$$

The second part diverges for $\rho \to 0$.

For the general solution we perform the following polynomial ansatz

$$P = \rho^{l+1}\sum_{k=0} a_k\rho^k = \rho^{l+1}L(\rho) \tag{8.123}$$

This ansatz has the correct asymptotic behaviour for $\rho \to 0$. Inserting this ansatz into the differential equation we are led to the relation

$$\begin{aligned}\sum_k a_k(l+1+k)(l+k)\rho^{l+k-1} - 2\alpha(l+1+k)a_k\rho^{l+k} + 2a_k\rho^{l+k}\\ -(l+1)la_k\rho^{l+k-1} = 0\end{aligned} \tag{8.124}$$

The corresponding recursion relation reads

$$\sum_k a_k\{(l+1+k)(l+k)-l(l+1)]\rho^{l+k-1}-2[\alpha(l+1+k)-1]a_k\rho^{l+k}\} = 0 \tag{8.125}$$

$$a_{k+1} = \frac{2[\alpha(l+k+1)-1]}{(l+k+2)(l+k+1)-l(l+1)}a_k \tag{8.126}$$

The Taylor expansion (8.123) stops at order K, provided we require

$$\alpha(l+K+1) - 1 = 0 \tag{8.127}$$

This requirement determines the energy eigenvalues

$$\epsilon = -\alpha^2 = -\frac{1}{(l+K+1)^2} \tag{8.128}$$

We can label the eigenvalues and eigenfunctions introducing the *principal quantum number n*

$$n = l + K + 1 \qquad , \qquad n = 1, 2, ... \tag{8.129}$$

n=1	K=0	l=0
n=2	K=0 K=1	l=1 l=0
n=3	K=0 K=1 K=2	l=2 l=1 l=0

The quantum number of angular momentum l is restricted to the principal quantum number

$$l = 0, 1, .., n - 1 \tag{8.130}$$

Magnetic quantum number m

$$-l, -l + 1, ..., 0, ...l - 1, l \tag{8.131}$$

8.5.3 Associate Laguerre Polynomials

The ansatz (8.123) introduces the so-called associate Laguerre polynomials $L(\rho)$. Inserting this ansatz into the differential equation (8.120) yields

$$\rho L'' + [2(l + 1) - 2\alpha\rho]L' - [2\alpha(l + 1) - 2]L = 0 \tag{8.132}$$

The transformation

$$\rho = \frac{x}{2\alpha} \tag{8.133}$$

The so-called associate Laguerre differential equation is obtained by considering that $\alpha = \frac{1}{n}$. Furthermore, we perform the transformation

$$\rho = \frac{\alpha}{2}x \tag{8.134}$$

This leads us to the so-called associate Laguerre differential equation

$$x\frac{d^2}{dx^2}L(x) + [(2l+1)+1-x]\frac{d}{dx}L(x) + [(n+l)-(2l+1)]L_{n+l}^{2l+1}(x) = 0 \tag{8.135}$$

The solutions of this differential equation are the associate Laguerre polynomials $L_{n+l}^{2l+1}(x)$.

Thus, the radial eigenfunctions $R_{nl}(r)$ can be constructed from the associate Laguerre polyonials:

$$R_{nl}(r) = N_{nl}(\frac{r}{a})^l L_{n+l}^{2l+1}(2\frac{r}{na}) \tag{8.136}$$

Rodrigues formula

$$L_{n+l}^{2l+1} = \left(-\frac{d}{dx}\right)^{2l+1} e^x \left(-\frac{d}{dx}\right)^{n+l} e^{-x}x^{n+l} \tag{8.137}$$

8.5.4 Summary: Energy Levels and Wave Functions

The energy eigenvalues (energy levels) depend on the principal quantum number n

$$E_n = R_H\epsilon = -R_H\frac{1}{n^2} \tag{8.138}$$

where R_H denotes the Rydberg constant. These energy levels are degenerate with respect to the quantum number of angular momentum l, whereas $l = 0,..,n-1$ and furthermore, with respect to the magnetic quantum number $m = -l,..,l$

The wave functions depend on the principal quantum number n, the quantum number of angular momentum l and the magnetic quantum number m.

$$\psi_{n,l,m}(r,\theta,\varphi) = |n,l,m>= R_{n,l}(\frac{r}{a})Y_{lm}\theta,\varphi \tag{8.139}$$

$$\begin{aligned}
R_{1,0} &= 2a^{-3/2}e^{-\rho} \\
R_{2,0} &= (2a)^{-3/2}(2-\rho)e^{-\rho/2} \\
R_{2,1} &= 3^{-1/2}(2a)^{-3/2}\rho e^{-\rho/2} \\
R_{3,0} &= 2(3a)^{-3/2}[1-\frac{2}{3}\rho+\frac{2}{27}\rho^2]e^{-\rho/3} \\
R_{3,1} &= \frac{4\sqrt{2}}{9}(3a)^{-3/2}\rho[1-\frac{1}{6}\rho]e^{-\rho/3} \\
R_{3,2} &= \frac{2\sqrt{2}}{27\sqrt{5}}(3a)^{-3/2}\rho^2e^{-\rho/3}
\end{aligned} \tag{8.140}$$

8.5.5 Associate Laguerre Functions

8.5.6 Symmetry and the Spectrum of the Hydrogen Atom

The degeneracy of the energy eigenvalues with respect to the magnetic quantum number is the result of the spherical symmetry. This becomes evident by the form of the Hamiltonian, which only depends on $\mathbf{L}^2$, but not on L_z.

8.5.7 Runge-Lenz-Vector

The degeneracy of the energy eigenvalues with respect to the quantum number of angular momentum is also related to a conservation law. The Runge Lentz vector is defined as

$$\mathbf{A} = \dot{\mathbf{r}} \times \mathbf{L} - \gamma\frac{\mathbf{r}}{r} \tag{8.141}$$

It is straightforward to show that the Runge Lentz vector $\mathbf{A}$ is a constant of motion, i.e.

$$\frac{d}{dt}\mathbf{A} = 0 \tag{8.142}$$

8.6 Alkali-Atoms

The Alkali atoms Lithium, Natrium, Kalium, Rubidium, Caesium, Franzium exhibit spectra which are quite similar to the spectrum of the Hydrogen atom. This is related to the fact that they have a single valence electron. A naive picture of such an atom is one, in which the positively charged core with charge Z e is surrounded by a cloud of (Z-1) electrons and a single valence electron. If the valence electron has orbits which are far away from the core and the (Z-1) electrons, the behaviour should be quite similar to the hydrogen atom, i.e. the potential energy of the valence electron would be equal to

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{8.143}$$

However, if this electron comes close to the core, the potential energy changes to

$$V(r) = -\frac{Ze^2}{4\pi\epsilon r} \tag{8.144}$$

As a consequence, the effective potential is not proportional to $1/r$. The degeneracy of the spectrum of the Hydrogen atom with respect to the quantum number l is broken. One expects the following dependency of the energy spectrum

$$E_{n,l} = -R\frac{1}{(n - \Delta(n,l))^2} \tag{8.145}$$

Here, the shift $\Delta(n,l)$ is due to the effective potential.

8.7 Appendix: Angular Momentum Operators and Spherical Coordinates

The coordinates x, y, z are related to spherical coordinates r, θ, φ according to

$$\begin{aligned} x &= rsin\theta cos\varphi \\ y &= rsin\theta sin\varphi \\ z &= rcos\theta \end{aligned} \tag{8.146}$$

Our aim is to determine the oprator of angular momenta in spherical coordinates.

We start by calculating the derivative with respect to φ:

$$\begin{aligned} \frac{\partial}{\partial\varphi} &= \frac{\partial x}{\partial\varphi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\varphi}\frac{\partial}{\partial y} + \frac{\partial z}{\partial\varphi}\frac{\partial}{\partial z} \\ &= -y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y} \end{aligned} \tag{8.147}$$

This operator is related to L_z:

$$L_z = \frac{\hbar}{i}[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}] = \frac{\hbar}{i}\frac{\partial}{\partial \varphi} \tag{8.148}$$

Next we calculate the derivative with respect to θ:

$$\begin{aligned}\frac{\partial}{\partial \theta} &= \frac{\partial x}{\partial \theta}\frac{\partial}{\partial x} + \frac{\partial y}{\partial \theta}\frac{\partial}{\partial y} + \frac{\partial z}{\partial \theta}\frac{\partial}{\partial z}\\ &= zcos\varphi\frac{\partial}{\partial x} + zsin\varphi\frac{\partial}{\partial y} - \frac{x}{\cos\varphi}\frac{\partial}{\partial z}\\ &= zcos\varphi\frac{\partial}{\partial x} + zsin\varphi\frac{\partial}{\partial y} - \frac{y}{\sin\varphi}\frac{\partial}{\partial z}\end{aligned} \tag{8.149}$$

Thus, we obtain

$$\begin{aligned}cos\varphi\frac{\partial}{\partial \theta} &= zcos^2\varphi\frac{\partial}{\partial x} + zsin\varphi cos\varphi\frac{\partial}{\partial y} - x\frac{\partial}{\partial z}\\ sin\varphi\frac{\partial}{\partial \theta} &= zcos\varphi sin\varphi\frac{\partial}{\partial x} + zsin^2\varphi\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\end{aligned} \tag{8.150}$$

Now,

$$\begin{aligned}cos\varphi\frac{\partial}{\partial \theta} &= z(cos^2\varphi - 1)\frac{\partial}{\partial x} + zsin\varphi cos\varphi\frac{\partial}{\partial y} + z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\\ sin\varphi\frac{\partial}{\partial \theta} &= zcos\varphi sin\varphi\frac{\partial}{\partial x} + z(sin^2\varphi - 1)\frac{\partial}{\partial y} + z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\end{aligned} \tag{8.151}$$

$$\begin{aligned}cos\varphi\frac{\partial}{\partial \theta} &= -zsin^2\varphi\frac{\partial}{\partial x} + zsin\varphi cos\varphi\frac{\partial}{\partial y} + z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\\ sin\varphi\frac{\partial}{\partial \theta} &= zcos\varphi sin\varphi\frac{\partial}{\partial x} - zcos^2\varphi\frac{\partial}{\partial y} + z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\end{aligned} \tag{8.152}$$

$$\begin{aligned}cos\varphi\frac{\partial}{\partial \theta} &= -ycot\theta sin\varphi\frac{\partial}{\partial x} + xcot\theta sin\varphi\frac{\partial}{\partial y} + z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\\ sin\varphi\frac{\partial}{\partial \theta} &= ycot\theta cos\varphi sin\varphi\frac{\partial}{\partial x} - xcot\theta cos\varphi\frac{\partial}{\partial y} + z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\end{aligned} \tag{8.153}$$

With the help of (8.147) we obtain

$$\begin{aligned}cos\varphi\frac{\partial}{\partial \theta} - cot\theta sin\varphi\frac{\partial}{\partial \varphi} &= z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\\ sin\varphi\frac{\partial}{\partial \theta} + cot\theta cos\varphi\frac{\partial}{\partial \varphi} &= z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\end{aligned} \tag{8.154}$$

The operators of angular momentum expressed in spherical coordinates are as follows:

$$\begin{aligned}
L_x &= \frac{\hbar}{i}[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}] \\
&= -\frac{\hbar}{i}[sin\varphi\frac{\partial}{\partial\theta} + cot\theta cos\varphi\frac{\partial}{\partial\varphi}] \\
L_y &= \frac{\hbar}{i}[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}] \\
&= \frac{\hbar}{i}[cos\varphi\frac{\partial}{\partial\theta} - cot\theta sin\varphi\frac{\partial}{\partial\varphi}] \\
L_z &= \frac{\hbar}{i}[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}] \\
&= \frac{\hbar}{i}\frac{\partial}{\partial\varphi} \qquad (8.155)
\end{aligned}$$

Using these representations we can determine $\mathbf{L}^2$:

$$\mathbf{L}^2 = -\hbar^2\{\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta} + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\} \qquad (8.156)$$

9

Diatomic Molecule

We consider a diatomic molecule. The two atoms form a molecule due to the binding forces resulting from the motion of electrons around the atoms. We will take this biding force into account in a phenomenological way postulating the existence of an attractive force between the two atoms, which we characterize by the potential $V(r)$. This potential will have the form depicted in figure (). Frequently, it can be approximated by the so-called Morse potential

$$V(r) = V_0(1 - e^{-(r-r_0)/a}) \tag{9.1}$$

If we denote the masses and the locations of the atoms by m_i and $\mathbf{r}_i$ we obtain the Hamilton operator

$$H = -\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 + V(|\mathbf{r}_1 - \mathbf{r}_2|) \tag{9.2}$$

As described in a previous section we are able to separate the motion of the center of mass and the relative motion. The Hamiltonian for the relative motion reads

$$H = -\frac{\hbar^2}{2m}\Delta + V(r) \tag{9.3}$$

As a result, we have reduced the problem of a molecule consisting of two atoms by the motion in a central force field given by the potential $V(r)$. The Hamiltonian reads

$$H = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{\mathbf{L}^2}{2mr^2} + V(r) \tag{9.4}$$

We assume that the oscillations around the equlibrium position R are small so that we can make the transformation

$$r = R + x \tag{9.5}$$

In lowest order we obtain the Hamiltonian

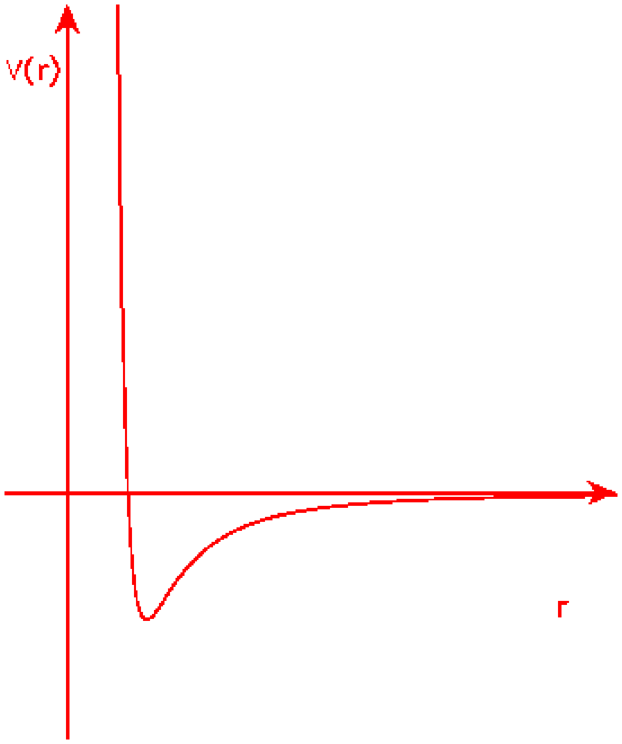


Fig. 9.1. Potential energy of the binding force of a diatomic molecule

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{m\omega^2}{2}x^2 + \frac{\mathbf{L}^2}{2J} \tag{9.6}$$

where we have introduced the momentum of inertia

$$J = mR^2 \tag{9.7}$$

The Hamiltonian consists of two parts. The first part is an harmonic oscillator, the second part is related to the rotation of the molecule.

The Hamiltonian is obtained under the assumption that the deviation x from the equilibrium position is small compared to the equilibrium distance R. This allows us to perform the following approximations

$$\frac{1}{(R+x)^2}\frac{\partial}{\partial x}(R+x)^2\frac{\partial}{\partial x} \approx \frac{\partial^2}{\partial x^2}$$

$$V(R+x) = V(R) + x\frac{\partial}{\partial R}V(R) \\ + \frac{1}{2}x^2\frac{\partial^2}{\partial R^2}V(R) = V(R) + \frac{m\omega^2}{2}x^2 \qquad (9.8)$$

Introducing creation and annihilation operators for the harmonic oscillator part we end up with the Hamiltonian

$$H = \hbar\omega[b^\dagger b + \frac{1}{2}] + \frac{\mathbf{L}^2}{2J} \qquad (9.9)$$

The corresponding energy eigenstates are obtained in a straightforward manner. A product ansatz yields the eigenstates

$$|n, l, m >= |n > |lm > \qquad (9.10)$$

or, in terms

$$\psi(x, \Theta, \varphi) = N_n H_n(x) e^{-\frac{x^2}{2}} Y_l^m(\Theta, \varphi) \qquad (9.11)$$

The energy spectrum takes the form

$$E_{n,l} = \hbar\omega(n + \frac{1}{2}) + \frac{\hbar^2 l(l+1)}{2J} \qquad (9.12)$$

The spectrum is degenerate with respect to the quantum number m.

It turns out that the quantity

$$\frac{\hbar^2}{2J} << \hbar\omega \qquad (9.13)$$

A schematic picture of the eigenstates are given in fig.

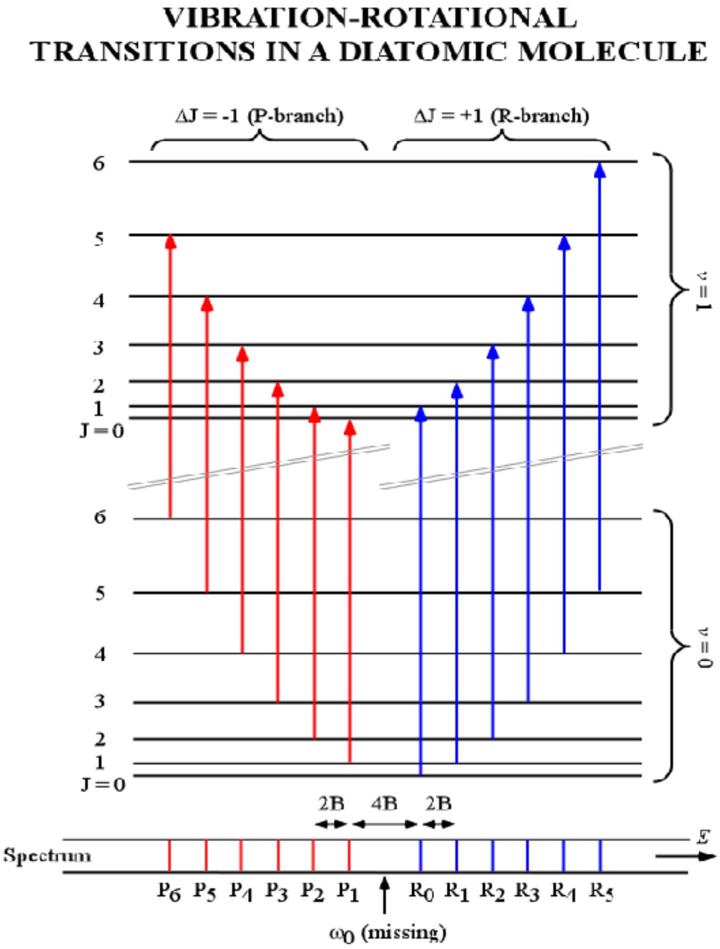


Fig. 9.2. Vibrational rotational spectrum of a diatomic molecule

10

Perturbation Theory

Only very few problems in quantum mechanics can be treated exactly. Examples are the harmonic oscillator or the Hydrogen atom. In order to deal with other systems of interest, e.g. the Hydrogen atom in an external electric field, one has to ressort to approximations applying so-called perturbation theory.

In this section we are concerned with time independent perturbation theory. The general outline of the problem is as follows:

We have to solve the time independent Schrödinger equation for a Hamiltonian whih is composed of the operator H_0, whose eigenvalue problem can be solved explicitly, and a perturbation V:

$$[H_0 + \epsilon V]|\psi >= E|\psi > \tag{10.1}$$

A smallness parameter ϵ is introduced in order to enumerate the arising terms of order $1 = \epsilon^0$, ϵ, ϵ^2 ....

One assumes that the eigenvalue $E = E(\epsilon)$ and the eigenvector $|\psi >= |\psi(\epsilon) >$ are smooth functions of ϵ, which are known for $\epsilon = 0$. Perturbation theory is devoted to the calculation of the corrections, which arise for small perturbations ϵV

$$\begin{aligned} E &= E^0 + \epsilon E^1 + \epsilon^2 E^2 + ... \\ |\psi > &= |\psi^0 > +\epsilon|\psi^1 > +\epsilon^2|\psi^2 > +... \end{aligned} \tag{10.2}$$

If we have , for $\epsilon = 0$, a nondegenerate eigenvalue, we expect a shift of this value. In the case of degen

10.1 Introductory Example

We consider the eigenvalue problem

$$H|\psi >= [H_0 + \epsilon W]|\psi >= E|\psi > \tag{10.3}$$

with the symmetric 2 × 2 matrices

$$H_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \quad , \quad W = \begin{pmatrix} W_1 & w \\ w & W_2 \end{pmatrix} \tag{10.4}$$

The eigenvalue problem is then related to the solution of the linear homogeneous system

$$\begin{pmatrix} E_1 + \epsilon W_1 - E & \epsilon w \\ \epsilon w & E_2 + \epsilon W_2 - E \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = 0 \tag{10.5}$$

Nontrivial solutions are obtained provided

$$\begin{aligned} Det(H_0 + \epsilon W - EI) &= (E_1 + \epsilon W_1 - E)(E_2 + \epsilon W_2 - E) - \epsilon^2 w^2 \\ &= E^2 - (E_1 + E_2 + \epsilon(W_1 + W_2))E \\ &+ (E_1 + \epsilon W_1)(E_2 + \epsilon W_2) - \epsilon^2 w^2 = 0 \end{aligned} \tag{10.6}$$

The characteristic equation can be solved

$$E_{1,2} = \frac{E_1^0 + E_2^0 + \epsilon(W_1 + W_2)}{2} \pm \sqrt{\frac{(E_1^0 - E_2^0 + \epsilon(W_1 - W_2))}{4} + \epsilon^2 w^2} \tag{10.7}$$

In order to obtain the eigenvalues for small values of ϵ, we can expand into a Taylor series with respect to the smallness parameter ϵ. To first order in ϵ we obtain

$$\begin{aligned} E_1 &= E_1^0 + \epsilon W_1 \\ E_2 &= E_2^0 + \epsilon W_2 \end{aligned} \tag{10.8}$$

To second order in ϵ^2 the result reads

$$\begin{aligned} E_1 &= E_1^0 + \epsilon W_1 + \epsilon^2 \frac{w^2}{2(E_1 - E_2)} \\ E_2 &= E_2^0 + \epsilon W_2 + \epsilon^2 \frac{w^2}{2(E_2 - E_1)} \end{aligned} \tag{10.9}$$

10.2 Perturbation Theory: Nondegenerate Case

In this section we shall generalize the above result to the time independent Hamilton operator:

$$[H_0 + \epsilon V]|\psi >= E|\psi > \tag{10.10}$$

We assume that the eigenfunctions $|n >$ and the eigenvalues E_n of the Hamiltonian H_0 are well-known:

$$H_0|n >= E_n^0|n > \tag{10.11}$$

In order to solve the linear eigenvalue problem we perform the following expansion

$$\begin{aligned} E &= E^0 + \epsilon E^1 + \epsilon^2 E^2 + ... \\ |\psi> &= |\psi^0> + \epsilon|\psi^1> + \epsilon^2|\psi^2> \end{aligned} \tag{10.12}$$

Inserting this ansatz into the eigenvalue problem and collecting terms of the same order in ϵ we find

$$\begin{aligned} &H_0|\psi^0> - E^0|\psi^0> = 0 \\ &H_0|\psi^1> - E^0|\psi^1> = -E^1|\psi^0> - V|\psi^0> \\ &H_0|\psi^2> - E^0|\psi^2> = -E^2|\psi^0> - E^1|\psi^1> - V|\psi^1> \end{aligned} \tag{10.13}$$

In general, one could write down the expansion in n-the order.

We shall now solve this set of equations order by order. In zeroth order we obtain the solution

$$E^0 = E^0_n \qquad , \qquad |\psi^0>=|n> \tag{10.14}$$

where we consider in detail a perturbation of the n-th eigenfunction corresponding to the eigenvalue E^0_n.

Let us now preceed to the solution of the first order equation

$$(H_0 - E^0_n)|\psi^1> = E^1|n> - V|n> \tag{10.15}$$

We can immediately determine the first order correction E^1_n to the energy value E^0_n by forming the scalar product of this equation with the eigenvector $|n>$:

$$<n|(H_0 - E^0_n)|\psi^1> = E^1 <n|n> - <n|V|n> \tag{10.16}$$

The left hand side, however is zero, since

$$<n|(H_0 - E^0_n)|\psi^1>=<(H_0 - E^0_n)n|\psi^1>=(E^0_n - E^0_n)<n|\psi>=0 \tag{10.17}$$

As a result, we obtain the first order correction

$$E^1_n =<n|V|n> \tag{10.18}$$

We proceed to determine the first order correction to the eigenvector, which is determined by eq. (10.15). To this end we perform an expansion of the first order correction $|\psi^1>$ in terms of the complete set of eigenvectors $|n>$

$$|\psi^1>=\sum_k c^k_n|k> \tag{10.19}$$

Equation (10.15) yields with the help of $H_0|k>=E^0_k|k>$

$$(H_0 - E_n^0)\sum_k c_n^k|k >= \sum_k (E_k^0 - E_n^0)c_n^k|k >= E_n^1|n > -V|n > \qquad (10.20)$$

Projecting this equation onto the eigenvector $|m >$ yields

$$\sum_k (E_k^0 - E_n^0)C_n^k < m|k >= E^1\delta_{mn} - < m|V|n > \qquad (10.21)$$

where we have exploited the fact that $< m|n >= \delta_{nm}$. We arrive at

$$(E_m^0 - E_n^0)c_n^m = E_n^1\delta_{mn} - < m|V|n > \qquad (10.22)$$

Again, we see that taking $n = m$ we obtain as solvability condition the first order correction $E_n^1 =< n|V|n >$. For $n \neq m$ we can determine the coefficients c_n^m:

$$c_n^m =< \frac{< m|V|n >}{E_n^0 - E_m^0} \qquad (10.23)$$

Thereby, we have to assume that $E_n^0 \neq E_m^0$, i.e. that we have no degeneracy of the energy spectrum. This case will be treated below.

We can now summarize our results to first order in ϵ

$$\begin{aligned} E &= E_n^0 + \epsilon E_n^1 = E_n^0 + \epsilon < n|V|n > \\ |\psi > &= |n > + \sum_m \frac{< m|V|n >}{E_n^0 - E_m^0}|m > \end{aligned} \qquad (10.24)$$

We shall proceed to the treatment of the second order corrections E_n^2 and $\psi_n^2 >$, which are determined by

$$H_0|\psi^2 > -E_n^0|\psi^2 > = E^2|n > +E^1|\psi^1 > -V|\psi^1 > \qquad (10.25)$$

Again, we can employ a solvability condition by forming the scalar product with $< n|$. The left hand side vanishes identically, whereas the right hand side yields the second order contribution

$$E^2 =< n|V|\psi_n^1 >= \sum_m < n|V|m > c_n^m =< \frac{| < m|V|n > |^2}{E_n^0 - E_m^0} \qquad (10.26)$$

We can now summarize our results to second order in ϵ

$$\begin{aligned} E &= E_n^0 + \epsilon < n|V|n > +\epsilon^2 \sum_{m \neq n} < \frac{| < m|V|n > |^2}{E_n^0 - E_m^0} \\ |\psi > &= |n > + \sum_m \frac{< m|V|n >}{E_n^0 - E_m^0}|m > \end{aligned} \qquad (10.27)$$

The second order contribution to the eigenvector can bed determined in a straightforward manner.

10.3 Perturbation Theory for Degenerate States

Example:

$$\begin{pmatrix} E^0 & \epsilon w \\ \epsilon w & E^0 \end{pmatrix} \tag{10.28}$$

Characteristic equation:

$$(E - E_0)^2 - \epsilon^2 w^2 = 0 \tag{10.29}$$

$$E = E_0 \pm \epsilon w \tag{10.30}$$

General: Finite dimensional subspace

$$H_0|n, \alpha >= E_n^0|n, \alpha > \tag{10.31}$$

Ansatz:

$$|\psi >= \sum_\alpha c_{n\alpha}|n\alpha > +\epsilon \sum_{k \neq n} |k\beta > +.. \tag{10.32}$$

$$\epsilon W \sum_\alpha c_{n\alpha}|n\alpha >= \epsilon E_n^1 \sum_\alpha c_{n\alpha}|n\alpha > \tag{10.33}$$

Projection

$$\sum_\alpha [< n\alpha|W|n\beta > -E_n^1 \delta_{\alpha,\beta}] c_{n\alpha} = 0 \tag{10.34}$$

11

Atoms in Electric Field

11.1 Application of Perturbation Theory

We consider the Hamilton operator of a Hydrogen atom in an electric field

$$H = H_0 + e\mathbf{r} \cdot \mathbf{E} \tag{11.1}$$

In order to approximately determine the energy levels we take the direction of the electric field as the z-direction and introduce spherical coordinates. As a result we obtain

$$H = H_0 + ercos\theta E \tag{11.2}$$

As we have seen in the section on time independent perturbation theory the various corrections are related to the matrix elements

$$< nlm|V|n'l'm' >=< nlm|rcos\theta|n'l'm' > \tag{11.3}$$

where the eigenfunctions of the Hamilton operator H_0 are denoted by

$$|nlm >= R_{nl}(r)Y_l^m(\theta, \varphi) \tag{11.4}$$

The explicit expression for the matrix elements

$$\begin{aligned} < nlm|rcos\theta|n'l'm' > = \int_0^\infty r^2 dr \int_0^\pi sin\theta d\theta \int_0^{2\pi} d\varphi R_{nl}(r) r R_{n'l'}(r) \\ \times Y_l^m(\theta, \varphi)^* cos\theta Y_{l'}^{m'}(\theta, \varphi) \end{aligned} \tag{11.5}$$

explicitly shows that the integrals factorizes according to

$$< nlm|V|n'l'm' >= M_{lm,l'm'} K_{nl,n'l'} \tag{11.6}$$

where the matrix elements $M_{lm,l'm'}$ involves integration with respect to the variables Θ, φ

$$M_{lm,l'm'} = \int_0^\pi sin\theta d\theta \int_0^{2\pi} d\varphi Y_l^m(\theta,\varphi)^* cos\theta Y_{l'}^{m'}(\theta,\varphi) \tag{11.7}$$

and a matrix element in volving the integral

$$K_{nl,n'l'} = \int_0^\infty r^2 dr R_{n'l'}(r) r R_{nl}(r) \tag{11.8}$$

It is convenient to represent $cos\theta$ as a spherical harmonics according to

$$cos\theta = \sqrt{\frac{4\pi}{3}} Y_1^0(\theta,\varphi) \tag{11.9}$$

As a consequence, one has to evaluate the integrals

$$\begin{aligned} M_{lm,l'm'} &= \int_0^\pi sin\theta d\theta \int_0^{2\pi} d\varphi Y_l^m(\theta,\varphi)^* Y_1^0(\theta,\varphi) Y_{l'}^{m'}(\theta,\varphi) \\ &= < Y_l^m | Y_{l'}^{m'} Y_1^0 > \end{aligned} \tag{11.10}$$

We emphasize that this matrix element is an example of a *Clebsch-Gordon coefficient.*

Due to the fact that

$$Y_l^m = e^{im\varphi} L_{lm}(cos\theta) \tag{11.11}$$

where L_{lm} are polynomial functions of $\cos\theta$ we immediately obtain the selection rule with respect to the quantum number m:

$$M_{lm;l'm'} = \delta_{m,m'} M_{lm;l'm'} \tag{11.12}$$

Furthermore, there are selection rules with respect to l,l'. It can be shown that $M_{lm,l'm'}$ is different from zero only in the cases

$$l = l' + 1 \qquad l = l' - 1 \tag{11.13}$$

11.2 Stark Effect of the Ground State n=1,l=0

We remind the reader that

$$Y_0^0(\theta,\varphi = \frac{1}{\sqrt{4\pi}} \tag{11.14}$$

As a consequence, the matrix element

$$\begin{aligned} M_{l,m;00} &= \delta_{m,0} \int_0^\pi sin\theta d\theta \int_0^{2\pi} d\varphi Y_l^m(\theta,\varphi)^* \sqrt{\frac{4\pi}{3}} Y_1^0(\theta,\varphi) \frac{1}{\sqrt{4\pi}} \\ &= \delta_{l,1} \delta_{m,0} \frac{1}{\sqrt{3}} \end{aligned} \tag{11.15}$$

can be evaluated using the orthogonality condition of the spherical harmonics:

$$< Y_l^m(\theta,\varphi) Y_1^{m'}(\theta,\varphi) = \delta_{ll'}\delta_{mm'} \tag{11.16}$$

In order to apply perturbation theory we have to consider the following matrix elements which are given by the following integrals:

$$< nlm|rcos\theta|100 >= \delta_{l,1}\delta_{m,0}\frac{1}{\sqrt{3}}\int_0^\infty r^2 dr R_{n1} r R_{10} \tag{11.17}$$

We are now in the position to determine the corrections to the ground state $|1,0,0>$ of the hydrogen atom. The first order contribution vanishes

$$E_{100}^1 =< 100|rcos\theta|100 >= M_{00,00}K_{10,10} = 0 \tag{11.18}$$

since $M_{00,00} = 0$, according to (11.17). As a result, the ground state of the hydrogen atom does not exhibit the linear Stark effect.

We proceed to calculate the second order correction to the energy eigenvalue E_1^0, which is given by

$$E_{100}^2 = e^2E^2\sum_{n,l}\frac{| < nl0|rcos\theta|100 > |^2}{E_{100}-E_{nl0}} \tag{11.19}$$

Due to the selection rule (11.17) only the matrix elements with l=1 contribute and we obtain explicitly

$$E_{100}^2 = e^2E^2\sum_n \frac{1}{3}\frac{|K_{n1,10}|^2}{E_{100}-E_{nl0}} \tag{11.20}$$

with the integrals

$$K_{n1,00} = \int_0^\infty r^2 dr r R_{n1}(r) R_{10}(r) \tag{11.21}$$

involving the (normalized) radial functions of the Hydrogen problem.

Taking the contribution with n=2 and neglecting the contirbutions from the higher order functions $R_{n1}(r)$ we obtain our final estimate for the second order contirbutions

$$E_{100}^{(2)} = -\frac{9}{4}a_B^3E^2e^2 \tag{11.22}$$

We can summarize: The ground state of the Hydrogen atom exhibits the quadratic Stark effect.

11.2.1 Induced Dipole Moment

Energy of a dipol in the electric field:

$$\Delta E = -\int d(E)dE = -\frac{\alpha}{2}E^2 = -\frac{d}{2}E \tag{11.23}$$

As a consequence:

$$< d >= \frac{9}{2}Ea_B^3 \tag{11.24}$$

Polarization

$$P = \rho < d >= \chi_e E \tag{11.25}$$

11.3 Linear Stark Effect

The linear Stark effect arises for the case of a degenerate energy level. We consider the states with principal quantum number $n = 2$. The energy level $E_2^0 = -Ry/4$ is fourfold degenerate and we denote the corresponding eigenstates by $|n\alpha >$, according to our notation in the section on perturbation theory:

$$\begin{aligned} |2,1> &= |2,0,0> \\ |2,2> &= |2,1,0> \\ |2,3> &= |2,1,1> \\ |2,4> &= |2,1,-1> \end{aligned} \tag{11.26}$$

In order to calculate the splitting of the degeneracy by the external electric field we have to calculate the matrix elements

$$< 2\alpha|rcos\theta|2\beta > \tag{11.27}$$

Due to selection rules only the matrix elements

$$< 22|rcos\theta|20 >= W =< 20|rcos\theta|22 > \tag{11.28}$$

is different from zero. It is explicitly given by

$$W = M_{10,00}K_{21,20} \tag{11.29}$$

with

$$M_{10,00} = \frac{1}{\sqrt{3}} \tag{11.30}$$

and

$$K_{21,20} = \int r^2 drrR_{20}(r)R_{21}(r) = \int_0^\infty r^2 dr\frac{2}{\sqrt{3}(2a)^3}e^{-r/a}(1-\frac{r}{a})\frac{r}{a}r \tag{11.31}$$

The radial wave functions are given by

$$R_{20} = \frac{2}{(2a)^{3/2}}(1-\rho)e^{-\rho/2}$$

$$R_{21} = \frac{1}{\sqrt{3}}\frac{1}{(2a)^{3/2}}\rho e^{-\rho} \tag{11.32}$$

a: Bohr's radius
As a consequence we obtain

$$W = 3eaE \tag{11.33}$$

Let us now consider the perturbation theory in first order. We make the following ansatz for the eigenvector

$$\begin{aligned} |\psi> &= \sum_{\alpha=1}^{4} c_2^\alpha |2\alpha> \\ &= c_1|200> + c_2|210> + c_3|211> + c_4|21-1> \end{aligned} \tag{11.34}$$

We obtain the following eigenvalue problem

$$\sum_{\beta=1}^{4} < 2\alpha|V|2\beta > c_2^\beta = E_2^1 c_2^\alpha \tag{11.35}$$

Explicitly,

$$\begin{pmatrix} 0 & W & 0 & 0 \\ W & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E_2^1 \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \tag{11.36}$$

This linear set of equations has only nontrivial solutions for eigenvalues E_2^1 determined by the characteristic equation

$$Det[< 2\alpha|V|2\beta > - E_2^1 \delta_{\alpha\beta}] = 0 \tag{11.37}$$

The characteristic equation reads

$$(E_2^1)^2(E_2^1 - W^2) = 0 \tag{11.38}$$

with the four roots

$$E_2^1 = 0 \quad , \quad E_2^1 = 0 \quad , \quad E_2^1 = W \quad , \quad E_2^1 = -W \tag{11.39}$$

In first order the energy eigenvalues split into three groups. The states $|2,1,1>$ and $|21-1>$ remain degenerate and there is not change of the eigenvalue in lowest order. The states $|210>$ and $|200>$ are coupled by the external field and the energy eigenvalues split:

$$\begin{aligned} E^1 &= 3eaE \qquad |\psi>= \frac{1}{\sqrt{2}}[|210> + |200>] \\ E^2 &= -3eaE \qquad |\psi>= \frac{1}{\sqrt{2}}[|210> - |200>] \end{aligned} \tag{11.40}$$

The corresponding eigenstates (to lowest) order are linear superpositions.