Chapter 4

Schroedinger Equation

Einstein's relation between particle energy and frequency Eq.(3.83) and de Broglie's relation between particle momentum and wave number of a corresponding matter wave Eq.(3.84) suggest a wave equation for matter waves. This search for an equation describing matter waves was carried out by Erwin Schroedinger. He was successful in the year 1926.

The energy of a classical, nonrelativistic particle with momentum $\vec{p}$ that is subject to a conservative force derived from a potential $V(\vec{r})$ is

$$E = \frac{\vec{p}^{\,2}}{2m} + V(\vec{r}). \tag{4.1}$$

For simplicity lets begin first with a constant potential $V(\vec{r}) = V_0 = \text{const}$. This is the force free case. According to Einstein and de Broglie, the dispersion relation between ω and $\vec{k}$ for waves describing the particle motion should be

$$\hbar\omega = \frac{\hbar^2\vec{k}^2}{2m} + V_0. \tag{4.2}$$

Note, so far we had a dispersion relation for waves in one dimension, where the wavenumber $k(\omega)$, was a function of frequency. For waves in three dimensions the frequency of the wave is rather a function of the three components of the wave vector. Each wave with a given wave vector $\vec{k}$ has the following time dependence

$$e^{\mathrm{j}\left(\vec{k}\cdot\vec{r}-\omega t\right)}, \text{ with } \omega = \frac{\hbar\vec{k}^2}{2m} + \frac{V_0}{\hbar} \tag{4.3}$$

Note, this is a wave with phase fronts traveling to the right. In contrast to our notation used in chapter 2 for rightward traveling electromagnetic waves, we switched the sign in the exponent. This notation conforms with the physics oriented literature. A superposition of such waves in $\vec{k}-$space enables us to construct wave packets in real space

$$\Psi(\vec{r}, t) = \int \phi_\omega\left(\vec{k}, \omega\right) \; e^{\mathrm{j}\left(\vec{k}\cdot\vec{r}-\omega t\right)} d^3k \; d\omega \tag{4.4}$$

The inverse transform of the above expression is

$$\phi_\omega\left(\vec{k}, \omega\right) = \frac{1}{(2\pi)^4} \int \Psi(\vec{r}, t)\, e^{-\mathrm{j}\left(\vec{k}\cdot\vec{r}-\omega t\right)} d^3r \; dt, \tag{4.5}$$

with

$$\phi_\omega\left(\vec{k}, \omega\right) = \phi(k) \;\; \delta\left(\omega - \frac{\hbar\vec{k}^2}{2m} - \frac{V_0}{\hbar}\right). \tag{4.6}$$

Or we can rewrite the wave function in Eq.(4.4) by carrying out the trivial frequency integration over ω

$$\Psi(\vec{r}, t) = \int \phi(k) \;\; \exp\left(\mathrm{j}\left[\vec{k}\cdot\vec{r} - \left(\frac{\hbar\vec{k}^2}{2m} + \frac{V_0}{\hbar}\right) t\right]\right) \; d^3k. \tag{4.7}$$

Due to the Fourier relationship between the wave function in space and time coordinates and the wave function in wave vector and frequency coordinates

$$\phi_\omega\left(\vec{k}, \omega\right) \;\; \leftrightarrow \;\; \Psi(\vec{r}, t) \tag{4.8}$$

we have

$$\omega \; \phi_\omega(k, \omega) \;\; \leftrightarrow \;\; \mathrm{j}\frac{\partial\Psi(\vec{r}, t)}{\partial t} \quad , \tag{4.9}$$

$$\vec{k} \; \phi_\omega(k, \omega) \;\; \leftrightarrow \;\; -\mathrm{j}\nabla\,\Psi(\vec{r}, t) \quad , \tag{4.10}$$

$$\vec{k}^2 \; \phi_\omega(k, \omega) \;\; \leftrightarrow \;\; -\Delta\;\Psi(\vec{r}, t) \quad . \tag{4.11}$$

where

$$\nabla = \vec{e}_{\mathrm{x}}\frac{\partial}{\partial x} + \vec{e}_{\mathrm{y}}\frac{\partial}{\partial y} + \vec{e}_{\mathrm{z}}\frac{\partial}{\partial z} \quad , \tag{4.12}$$

$$\Delta = \nabla\cdot\nabla \equiv \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{4.13}$$

From the dispersion relation follows by multiplication with the wave function in the wave vector and frequency domain

$$\hbar\,\omega\,\phi_\omega\,(k,\omega) = \frac{\hbar^2 k^2}{2m}\phi_\omega\,(k,\omega) + V_0\,\phi_\omega\,(k,\omega) \quad . \tag{4.14}$$

With the inverse transformation the corresponding equation in the space and tieme domain is

$$\mathrm{j}\,\hbar\frac{\partial\Psi\,(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\Delta\ \Psi\,(\vec{r},t) + V_0\ \Psi\,(\vec{r},t) \ \ . \tag{4.15}$$

Generalization of the above equation for a constant potential to the instance of an arbitrary potential in space leads finally to the Schroedinger equation

$$\mathrm{j}\,\hbar\frac{\partial\Psi\,(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\Delta\ \Psi\,(\vec{r},t) + V\,(\vec{r})\ \ \Psi\,(\vec{r},t) \ \ . \tag{4.16}$$

Note, the last few pages ar not a derivation of the Schroedinger Equation but rather a motivation for it based on the findings of Einstein and deBroglie. The Schroedinger Equation can not be derived from classical mechanics. But classical mechanics can be rederived from the Schroedinger Equation in some limit. It is the success of this equation in describing the experimentally observed quantum mechanical phenomena correctly, that justifies this equation.

The wave function $\Psi\,(\vec{r},t)$ is complex. Note, we will no longer underline complex quantities. Which quantities are complex will be determined from the context.

Initially the magnitude square of the wave function $|\Psi\,(\vec{r},t)|^2$ was interpreted as the particle density. However, Eq.(4.15) in one spatial dimension is mathematical equivalent to the dispersive wave motion Eq.(2.72), where the space and time variables have been exchanged. The dispersion leads to spreading of the wave function. This would mean that any initially compact particle, which has a well localized particle density, would decay, which does not agree with observations. In the framwork of the "Kopenhagen Interpretation" of Quantum Mechanics, whose meaning we will define later in detail, $|\Psi\,(\vec{r},t)|^2\,dV$ is the probability to find a particle in the volume dV at position $\vec{r}$, if an optimum measurement of the particle position is carried out at time t. The particle is assumed to be point like. $\Psi\,(\vec{r},t)$ itself is then considered to be the probability amplitude to find the particle at position $\vec{r}$ at time t.

Note, that the measurement of physical observables like the position of a particle plays a central role in quantum theory. In contrast to classical mechanics where the state of a particle is precisely described by its position and momentum in quantum theory the full information about a particle is represented by its wave function $\Psi(\vec{r}, t)$. $\Psi(\vec{r}, t)$ enables to compute the outcome of a measurement of any possible observable related to the particle, like its position or momentum.

Before, we discuss this issue in more detail lets look at a few examples to get familiar with the mathematics of quantum mechanics.

4.1 Free Motion

Eq.(4.15) describes the motion of a free particle. For simplicity, we consider only a one-dimensional motion along the x-axis. Initially, we might only know the position of the particle with finite precision and therefore we use a Gaussian wave packet with finite width as the initial wave function

$$\Psi(x, t=0) = A \ \exp\left(-\frac{x^2}{4\sigma_0^2} + \mathrm{j}k_0 x\right). \tag{4.17}$$

The probability density to find the particle at position x is a Gaussian distribution

$$|\Psi(x, t=0)|^2 = |A|^2 \ \exp\left(-\frac{x^2}{2\sigma_0^2}\right), \tag{4.18}$$

σ_0^2 is the variance of the initial particle position. Since the probability to find the particle somewhere must be one, we can determine the amplitude of the wave function by requireing

$$\int_{-\infty}^{\infty} |\Psi(x, t=0)|^2 \, dx = 1 \rightarrow A \ = \frac{1}{\sqrt[4]{2\pi}\sqrt{\sigma_0}} \tag{4.19}$$

The meaning of the wave number k_0 in the wave function (4.17) becomes obvious by expressing the solution to the wave equation by its Fourier transform

$$\Psi(x, t) = \int_{-\infty}^{+\infty} \phi(k) \exp \quad \mathrm{j}(kx - \omega(k)\, t) \ \ dk \tag{4.20}$$

or specifically for $t = 0$

$$\Psi(x,0) = \int_{-\infty}^{+\infty} \phi(k)\, e^{\mathrm{j}kx}\, dk\,, \tag{4.21}$$

or

$$\phi(k) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \Psi(x,0)\, e^{-\mathrm{j}kx}\, dx \quad . \tag{4.22}$$

For the initial Gaussian wavepacket of

$$\Psi(x,0) = A\ \exp\left(-\frac{x^2}{4\sigma_0^2} + \mathrm{j}k_0 x\right) \tag{4.23}$$

we obtain

$$\phi(k) = \frac{A\sigma_0}{\sqrt{\pi}} \exp\left[-\sigma_0^2 (k-k_0)^2\right] \quad . \tag{4.24}$$

This is a Gaussian distribution for the wave number, and therefore momentum, of the particle with its center at k_0. With the dispersion relation

$$\omega = \frac{\hbar\, k^2}{2\, m}\,, \tag{4.25}$$

with the constant potential V_0 set to zero, the wave function at any later time is

$$\Psi(x,t) = \frac{A\sigma_0}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \exp\left[-\sigma_0^2 (k-k_0)^2 - \mathrm{j}\frac{\hbar k^2}{2m} t + \mathrm{j}kx\right] dk. \tag{4.26}$$

This is exactly the same Gaussian integral we were studying for dispersive pulse propagation or the diffraction of a Gaussian beam in chapter 2 which results in

$$\Psi(x,t) = \frac{A}{\sqrt{1 + \mathrm{j}\frac{\hbar\, t}{m 2\sigma_0^2}}} \exp\left[-\frac{x^2 - 4\,\mathrm{j}\sigma_0^2 k_0\ x + \mathrm{j}\ \frac{\hbar 2\sigma_0^2 k_0^2}{m}\ t}{4\sigma_0^2\left(1 + \mathrm{j}\frac{\hbar}{m 2\sigma_0^2}\ t\right)}\right] \quad . \tag{4.27}$$

As expected the wave packet stays Gaussian. The probability density is

$$|\Psi(x,t)|^2 = \frac{|A|^2}{\sqrt{1 + (\frac{\hbar\, t}{2m\sigma_0^2}))}} \exp\left[-\frac{\left(x - \frac{\hbar\, k_0}{m}\ t\right)^2}{2\sigma_0^2\left[1 + \left(\frac{\hbar\, t}{2m\sigma_0^2}\right)^2\right]}\right] \quad . \tag{4.28}$$

With the value for the amplitude A according to Eq.(4.19), the wave packet remains normalized

$$\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \, dx = 1. \tag{4.29}$$

Using the probability distribution for the particle position, we obtain for its expected value

$$\langle x \rangle = \int_{-\infty}^{+\infty} x \ |\Psi(x,t)|^2 \, dx \tag{4.30}$$

or

$$\langle x \rangle = \frac{\hbar \ k_0}{m} t \quad . \tag{4.31}$$

Thus the center of the wave packet moves with the velocity of the classical particle

$$\upsilon_0 = \frac{\hbar \ k_0}{m}, \tag{4.32}$$

which is the group velocity derived from the dispersion relation (4.2)

$$\upsilon_0 = \left.\frac{\partial \omega(k)}{\partial k}\right|_{k=k_0} = \frac{1}{\hbar} \left.\frac{\partial E(k)}{\partial k}\right|_{k=k_0} . \tag{4.33}$$

As we will see later, the expected value for the center of mass of the particle follows Newton's law, which is called Ehrenfest's Theorem. For the uncertainty in the particle position

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \tag{4.34}$$

follows for the freely moving particle

$$\Delta x = \sigma_0 \sqrt{1 + \left(\frac{\hbar t}{2m\sigma_0^2} \right)^2} \quad . \tag{4.35}$$

The probability density for the particle position disperses over time. Asymptotically one finds

$$\Delta x \doteq \frac{\hbar t}{2m\sigma_0^2} \quad \text{for} \quad \frac{\hbar t}{2m\sigma_0^2} \gg 1 \quad . \tag{4.36}$$

Figure 4.1 (a) is a sketch of the complex wave packet and (b) indicates the temporal evolution of the average and variance of the particle center of mass motion described by the complex wave packet. The wave packet disperses faster, if it is initially stronger localised.

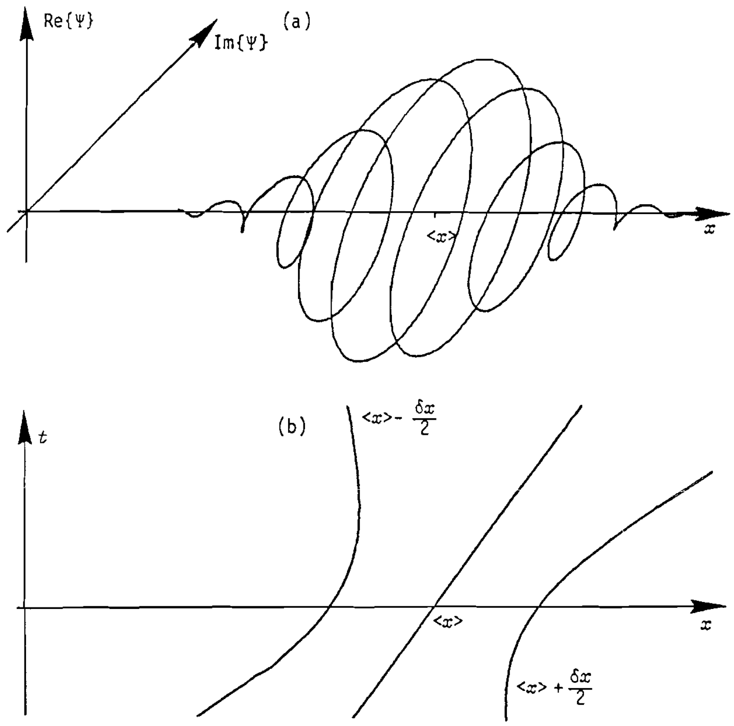

Figure 4.1: Gaussian wave packet: (a) Real and Imaginary part of the complex wave packet. (b) width and center of mass of the wave packet.

Example:

Using this one dimensional model, we can estimate how rapidly an electron moves in a hydrogen atom. If we localize an electron in a box with a size similar to that of a hydrogen atom, i.e. $\sigma_0 = a_0 = 0.5 \cdot 10^{-10} m$, without the presence of the proton that holds the electron back from escaping, it will only take $t = 2m\sigma_0^2/\hbar = 2 \cdot 9.81 \cdot 10^{-31}\text{kg} \cdot (0.5 \cdot 10^{-10})^2 \text{m}^2/6.626 \cdot 10^{-34}\text{Js} = 46.5\text{as}$ (attoseconds=10^{-18} sec) until its wave function disperses significantly. This result indicates that electronic motion in atoms occurs on a attosecond time scale. Note, these time scales quickly become very long if macroscopic objects are described quantum mechanically. For example, for a particle with a mass of 1μg localized in a box with dimensions $1\mu m$, the equivalent time for significant dispersion of the wave function is $t = 2 \cdot 10^{19}$s $= 2$Million years. This result gives us a first indication why we are far, far away from encountering quantum mechanical effects in our everyday life and why the mechanics of the micro cosmos, on an atomic or molecular level, is so different from our macroscopic experience. The reason is the smallness of the quantum of action h.

The reason for this behaviour is that a well localized particle has a wider momentum or wave number distribution. This is in one to one analogy that an otpical pulse disperses faster in a medium with a given dispersion if it is shorter because of larger spectral width. The wave number spread is

$$(\Delta k)^2 = \frac{\int\limits_{-\infty}^{\infty} (k - k_0)^2 \left|\phi(k)\right|^2 dk}{\int\limits_{-\infty}^{\infty} \left|\phi(k)\right|^2 dk} \quad . \tag{4.37}$$

Here, we have

$$\Delta k = \frac{1}{2\sigma_0}, \tag{4.38}$$

or for the momentum spread

$$\Delta p = \frac{\hbar}{2\sigma_0}. \tag{4.39}$$

The position-momentum uncertainty product is then

$$\Delta p \; \Delta x = \frac{\hbar}{2}\sqrt{1 + \left(\frac{\hbar\, t}{2m_0^2}\right)^2} \quad . \tag{4.40}$$

The position-momentum uncertainty product is a minimum at $t = 0$ and steadily increases from this initial value. As we will show later it is in generally true that the position-momentum uncertainty product satisfies the condition

$$\Delta x_\mathrm{i}\, \Delta p_\mathrm{i} \geqslant \frac{\hbar}{2}. \tag{4.41}$$

Note, that the index i indicates the coordinate. This is Heisenberg's uncertainy relation between particle position and moment, which holds for each component individually. Later, we will find other pairs of physical obser-vavles, which are called conjugate observables and which satiesfy similar uncertainty relations. The product of such quantities is always an action. This is for example also true for the product of energy and frequency and the resulting energy-time uncertainty relation is

$$\Delta E\,\Delta t \geqslant \frac{\hbar}{2}. \tag{4.42}$$

Note, whereas the position-momentum uncertainy is related to the choice of the particle state described by the wave function, the energy-time uncertainty relation is related to the dynamics of a quantum process. What it means is that a quantum system can only change its state significantly within a time span Δt, if the state, the quantum system is in, has an energy uncertainty larger than $\delta E \geqslant \frac{\hbar}{2\delta t}$.

Position and momentum variables that do not belong to the same degree of freedom, such as y, and p_x are not subject to an uncertainty relation.

4.2 Probability Conservation and Propability Currents

Max Born was the first to introduce the propabilistic interpretation of the wave function found by Schroedinger, that is the propability to find the center of mass of a particle at position $\vec{r}$ in a volume element dV is given by the magnitude square of the wave function multiplied by dV

$$p\left(\vec{r},t\right) = \left|\Psi\left(\vec{r},t\right)\right|^2 \mathrm{d}\,V \quad . \tag{4.43}$$

If this interpretation makes sense, then the total propability that the parti-cle can be found somewhere should by 1 and this normalization should not change during the dynamics. We found that this is true for the Gaussian wave packet undergoing free motion. Here, we want to show that this is true under the most general circumstances. We look at the rate of change of the probability to find the particle in an arbitrary but fixed volume $V = Vol$

$$\frac{d}{dt}\int_{Vol} p(\vec{r},t)\ d^3r = \tag{4.44}$$
$$= \int_{Vol} \frac{\partial}{dt}\left|\Psi(\vec{r},t)\right|^2\ d^3r$$
$$= \int_{Vol}\left[\left(\frac{\partial}{\partial t}\Psi^*(\vec{r},t)\right)\Psi(\vec{r},t) + \Psi^*(\vec{r},t)\left(\frac{\partial}{\partial t}\Psi(\vec{r},t)\right)\right] d^3r$$

Using the Schroedinger Equation (4.16) for the temporal change of the wave function we obtain

$$\frac{d}{dt}\int_{Vol} p(\vec{r},t)\ d^3r =$$
$$= \int_{Vol}\left[\left(\frac{\hbar}{j2m}\nabla\cdot\nabla\ \Psi^*(\vec{r},t) - \frac{j}{\hbar}V(\vec{r})\ {}^*\ \Psi^*(\vec{r},t)\right)\Psi(\vec{r},t)\right] d^3r \tag{4.45}$$
$$+ \int_{Vol}\left[\Psi^*(\vec{r},t)\left(-\frac{\hbar}{j2m}\nabla\cdot\nabla\ \ \Psi(\vec{r},t) + \frac{j}{\hbar}V(\vec{r})\ \ \Psi(\vec{r},t)\right)\right] d^3r$$

Since the potential $V(\vec{r})$ is real the terms related to it cancel. The other two terms can be written of the divergence of a current density

$$\int_{Vol}\frac{\partial}{\partial t}p(\vec{r},t)\ d^3r = -\int_{Vol}\nabla\cdot\vec{J}(\vec{r},t)\,d^3r, \tag{4.46}$$

with

$$\vec{J}(\vec{r},t) = \frac{\hbar}{j2m}\left(\Psi^*(\vec{r},t)\ \left(\nabla\Psi(\vec{r},t)\right) - \Psi(\vec{r},t)\left(\nabla\Psi^*(\vec{r},t)\right)\right). \tag{4.47}$$

Eq.(4.46) is true for any volume, i.e.

$$\int_{Vol}\left[\frac{\partial}{\partial t}p(\vec{r},t) + \nabla\cdot\vec{J}(\vec{r},t)\right]\ d^3r = 0, \tag{4.48}$$

which is only possible if the integrand vanishes

$$\frac{\partial}{\partial t}p(\vec{r},t) = -\ \nabla\cdot\vec{J}(\vec{r},t)\,. \tag{4.49}$$

Clearly, $\vec{J}(\vec{r},t)$ has the physical meaning of a probability current. The probability in a volume element changes because of probablity flowing out of this volume element. Note, this is the same local law that we have for the conservation of charge. In fact, if the particle is a charged particle, like an electron is, multiplication of $\vec{J}$ with $-e_0$ would result in the electrical current associated with the wave function $\Psi(\vec{r},t)$.

Gauss's theorem states

$$\int_{Vol} \nabla \cdot \vec{J}(\vec{r},t)\ d^3r = \int_S \vec{J}(\vec{r},t)\ d\vec{S}, \tag{4.50}$$

where Vol is the volume over which the integration is carried out and S is the surface that encloses the volume with $d\vec{S}$ an outward pointing surface normal vector. With Gauss's theorem the local conservation of probability can be transfered to a global result, since

$$\frac{d}{dt}\int_{Vol} p(\vec{r},t)\ d^3r = -\int_{Vol} \nabla \cdot \vec{J}(\vec{r},t)\, d^3r = -\int_S \vec{J}(\vec{r},t)\ d\vec{S}. \tag{4.51}$$

If we choose as the volume the whole space and if $\Psi(\vec{r},t)$ and $\frac{\partial}{\partial t}\Psi(\vec{r},t)$ vanish rapidly enough for $\vec{r} \to \infty$ such that the probability current vanishes at infinity, the total probability is conserved. These findings proove that the probabilty interpretation of the wave function is a valid interpretation not contradicting basic laws of probability. If the wave function properly normalized at the beginning it will stay normalized.

Example The Gaussian wave packet satisfies the condition that the probability current decays rapidly enough at the surface of a large enough chosen volume so that the normalization is preserved. A monochromatic plane wave does not satisfy this condition. However, the probability current density gives a physical meaning to it. The wave function corresponding to a plan wave

$$\Psi(\vec{r},t) = e^{\mathrm{j}\left(\vec{k}\cdot\vec{r}-\omega t\right)}, \text{ with } \omega = \frac{\hbar\vec{k}^2}{2m} + \frac{V_0}{\hbar} \tag{4.52}$$

which is not normalizable, results in a homogenous probability current

$$\begin{aligned} \vec{J}(\vec{r},t) &= \frac{\hbar}{j2m}\left(\Psi^*(\vec{r},t)\ \left(\nabla\Psi(\vec{r},t)\right) - \Psi(\vec{r},t)\left(\nabla\Psi^*(\vec{r},t)\right)\right) \quad (4.53)\\ &= \frac{\hbar\vec{k}}{m}\left|\Psi(\vec{r},t)\right|^2 = \frac{\vec{p}}{m} = \vec{v}, \end{aligned}$$

that is identical to the classical velocity of the particle. Thus a plane wave describes a particle with a precise velocity or momentum but completely unknown position, therefore the related probability current density is completely homogenous but directed into the direction of $\vec{v}$. Such waves describe the initial state in a scattering experiment, where we shoot particles with a precisely defined velocity $\vec{v}$ or momentum $\vec{p}$ or energy $E = \frac{m\vec{v}^2}{2} = \frac{\hbar\vec{p}^2}{2m} = \frac{\hbar\vec{k}^2}{2m}$ onto another object described by a scattering potential, see problem set. The position of these particles is completely unspecified, i.e. $|\Psi(\vec{r},t)|^2$ =const.

4.3 Measureability of Physical Quantities (Observables)

The reason for the more intricate description necessary for microscopic processes in comparison with macroscopic processes is simply the fact that these systems are so small that the interaction of the system with an eventual measurement apparatus can no longer be neglected. It turns out this fact is not to overcome by choosing more and more sophisticated measurement apparati but rather is a principle limitation. If this is so, then it eventually doesn't make sense or it becomes even inconsistent to attribute to a system more precisely defined physical quantities than actually can be retrieved by measurements. This is the physical reason behind the introduction of the wave function in stead of the precisely defined position and momentum of the particle that we used to deterministically predict the trajectory of a particle in an external field.

It is impossible to assign to a microscopic particle a precise position and momentum at the same time. To demonstrate this, we consider the following (Heisenberg) microscope to measure the exact position of a particle. We use light with wavelength λ and focus it strongly with a lense of some focal distance d, see Figure 4.2.

From our construction of the Gaussian beam in section 2.4.2, we found that if we generate a focused beam with a waist w_o having a Rayleigh range $z_R = \frac{\pi w_o^2}{\lambda}$, the beam is composed of plane waves which have a Gaussian distribution in its transverse k-vector, which has a variance $k_T^2/2$, see Eq.(2.220). The Rayleigh range of the beam is related to the transverse wave number spread of the beam by $z_R = k_0/k_T^2$, with $k_0 = 2\pi/\lambda$, see (2.221) and thereafter. Note, the intensity profile of the beam has a variance $w_o^2/4$. If a particle crosses the focus of the beam and scatters a single photon, which we detect with the surrounding photo detector arrangement, then it is reasonable to assume that we know the position of the particle in the x-direction, with an uncertainty equal to the uncertainty in the transverse photon or intensity distribution of the beam, i.e. $\Delta x = w_o\ /2$.

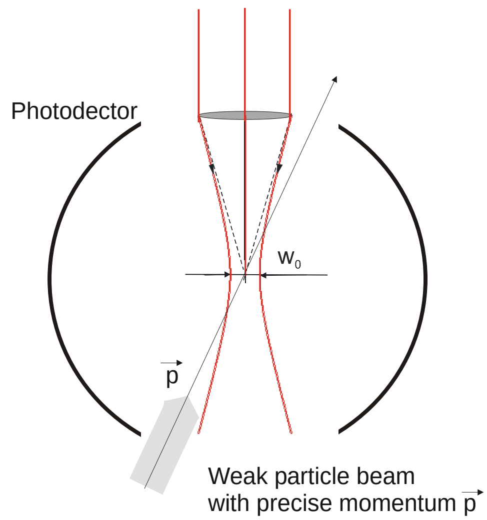

Figure 4.2: Determination of particle position with an optical microscope. A weak particle beam with precisely defined moment $\vec{p}$ of the particles is directed towards the focus of the Gaussian beam. In the focus the particle scatters at least one photon. Detection of the scattered photon with the surrounding photodetector signals, that the position of the particle in x-direction has been determined within the beam waist of the Gaussian beam. However, due to the scattering of the photon a momentum uncertainty has been introduced to the particle state.

During the measurement, the photon recoil induces a momentum kick with an uncertainty $\Delta p_x = \hbar k_T/\sqrt{2}$. So even if the momentum of the particle was perfectly know before the measurement, after the additional determination of its position with a precision Δx it has at least aquired an uncertainty in its momentum of magnitude Δp_x. The product of the uncertainties in postion and momentum after the measurement is

$$\Delta p_x \cdot \Delta x = \hbar k_T w_o / \left(2\sqrt{2}\right) = \frac{\hbar}{2}. \tag{4.54}$$

Note, this result is exact and is independent of focusing. Tighter focusing will enable us to more precisely determine the position of the particle, but we will introduce more momentum uncertainty due to the photon recoil; the opposite is true for less focusing. Since we can not determine, and therefore, prepare a particle in a state with its position and momentum more precisely determined than this uncertainty product allows, there is nowsuch state and (4.54) is the minimum uncertainty product achievable.

The experimental setup can easily be extended to measure the momentum and position of a particle in all three dimensions. For example one can use three focused laser beams at different wavelength, which are orthogonal to each other. Once a particle will fly through the focus and scatters three photons, each of different color. If we knew its momentum initially precisely, we would know afterwards its 3-dimensional position with a position and momentum spread as described by Eq.(4.54).

4.4 Stationary States

One of the great mysteries before the advent of quantum mechanics was the orgin of the discrete energy spectra observed in spectroscopic investigations and empirically described by the Bohr-Sommerfeld model of the atom. This mystery is easily explained by the Schroedinger Equation (4.16)

$$\mathrm{j}\,\hbar\frac{\partial\Psi\left(\vec{r},t\right)}{\partial t}=-\frac{\hbar^{2}}{2m}\Delta\;\Psi\left(\vec{r},t\right)+V\left(\vec{r}\right)\;\Psi\left(\vec{r},t\right)\;. \tag{4.55}$$

It allows for solutions

$$\Psi\left(\vec{r},t\right)=\psi\left(\vec{r}\right)\;e^{\mathrm{j}\,\omega t}, \tag{4.56}$$

which have a time independent probability density, i.e.

$$\left|\Psi\left(\vec{r},t\right)\right|^{2}=\left|\psi\left(\vec{r}\right)\right|^{2}=\mathrm{const.}, \tag{4.57}$$

which is the reason for calling these states stationary states. Since the right side of the Schroedinger Equation is equal to the total energy of the system, these states correspond to energy eigenstates of the system with energy eigenvalues

$$E=\hbar\omega. \tag{4.58}$$

These energy eigenstates $\psi(\vec{r})$ are eigen solutions to the stationary or time independent Schroedinger Equation

$$-\frac{\hbar^2}{2m}\Delta\ \psi(\vec{r}) + V(\vec{r})\ \psi(\vec{r}) = E\ \psi(\vec{r})\ . \tag{4.59}$$

We get familiar with this equation by considering a few one-dimensional examples, before we apply it to the Hydrogen atom.

4.4.1 The One-dimensional Infinite Box Potential

A simple example for a quantum mechanical system is an electron that can freely move in one dimension x but only over a finite distance a. Such a situation closely describes an electron that is strongly bound to a molecule with a cigar like shape with length a. The potential describing this situation is the one-dimensional box potential

$$V(x) = \begin{cases} 0, & \text{for } |x| < a/2 \\ \infty, & \text{for } |x| \geq a/2 \end{cases}, \tag{4.60}$$

see Figure 4.3.

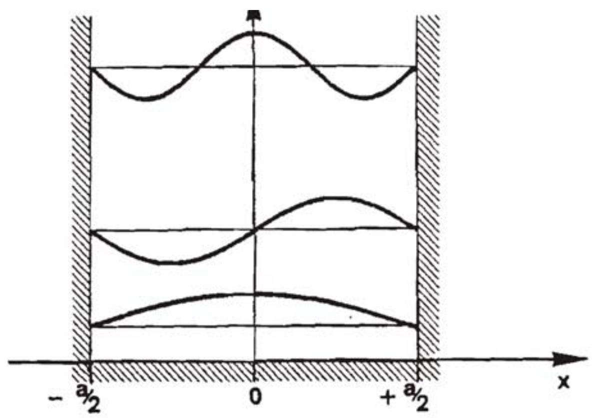

Figure 4.3: One dimensional box potential with infinite barriers.

In the interval $[-a/2, a/2]$ the stationary Schroedinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\ \psi(x)\,. \tag{4.61}$$

For $|x| \geq a/2$ the wave function must vanish, otherwise the energy eigenvalue can not be finite, i.e. $\psi\left(x = \pm a/2\right) = 0$. This is analogous to the electric field solutions for the TE-modes for a planar mirror waveguide and we find

$$\psi_n\left(x\right) = \sqrt{\frac{2}{a}} \; \cos \; \frac{n\pi x}{a} \quad \text{for} \quad n = 1, 3, 5 \ldots, \tag{4.62}$$

$$\psi_n\left(x\right) = \sqrt{\frac{2}{a}} \; \sin \; \frac{n\pi x}{a} \quad \text{for} \quad n = 2, 4, 6 \ldots. \tag{4.63}$$

The corresponding energy eigenvalues are

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}. \tag{4.64}$$

We also find that the stationary states constitute an orthogonal system of functions

$$\int_{-\infty}^{+\infty} \psi_m\left(x\right)^* \psi_n\left(x\right) dx = \delta_{mn}. \tag{4.65}$$

In fact this system is complete. Any function in the interval $[-a/2, a/2]$ can be expanded in a superposition of the basis functions $\psi_n\left(x\right)$, which is a Fourier series

$$f\left(x\right) = \sum_{n=0}^{\infty} c_n \psi_n\left(x\right) \tag{4.66}$$

with

$$c_m = \int_{-a/2}^{a/2} \psi_m\left(x\right)^* f\left(x\right) dx, \tag{4.67}$$

which is a consequence of the orthogonality relation (4.65).

Example: If we approximate the binding potential of a hydrogen atom by a one-dimensional box potential with a width equal to twice the Bohr radius $a = 2a_0 = 10^{-10}$m, the energy eigenvalues are $E_n = n^2 \cdot 35eV$. Clearly, the spacing of the energy eigenvalues does not conform with what has been observed experimentaly, compare with section 3.4, however the energy scale is within an order of magnitude. The ionization potential of the hydrogen atom is $13.5eV$.

4.4.2 The One-dimensional Harmonic Oscillator

The most important example of a quantum system is the one-dimensional harmonic oscillator. It is the most basic mechanical and electrical system and it describes the dynamics of a mode of the radiation field, see Figure 4.4.

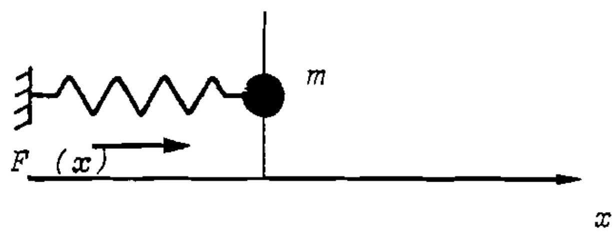

Figure 4.4: Elastically bound particle

Mechanically, a harmonic oscillation comes about by the elastic force obeying Hook's law

$$F(x) = -Kx, \tag{4.68}$$

that pulls back a particle with mass m in its equilibrium position. This force is conservative and can be derived from a potential by

$$F(x) = -\frac{\mathrm{d}\,V(x)}{\mathrm{d}x}, \tag{4.69}$$

with

$$V(x) = \frac{1}{2}\,Kx^2\,. \tag{4.70}$$

Newton's law results in the classical equation of motion

$$m\ddot{x} = F(x)\,, \tag{4.71}$$

or

$$\ddot{x} + \omega_0^2 x = 0, \tag{4.72}$$

with the oscillation frequency

$$\omega_0 = \sqrt{\frac{K}{m}} \tag{4.73}$$

The corresponding stationary Schroedinger Equation is

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}Kx^2\right)\ \psi(x) = 0. \tag{4.74}$$

This equation is well known in mathematical physics and we want to bring it into standardized form by the scale transformation, i.e. introducing a normalized distance

$$\xi = ax, \tag{4.75}$$

with the scale factor

$$a = \left(\frac{mK}{\hbar^2}\right)^{\frac{1}{4}} = \sqrt{\frac{\omega_0 m}{\hbar}} = \sqrt{\frac{K}{\hbar\omega_0}}. \tag{4.76}$$

In addition we introduce the energy scale factor

$$\gamma = \frac{2E}{\hbar\omega_0}. \tag{4.77}$$

Then the stationary Schroedinger Equation for the harmonic oscillator is

$$\frac{d^2\psi(\xi)}{d\xi^2} + \left(\gamma - \xi^2\right)\ \psi(\xi) = 0. \tag{4.78}$$

It turns out [4][6], that this equation has only solutions that are bounded, i.e. $\psi(\xi \rightarrow \pm\infty) = 0$, if the normalized energies are

$$\gamma_n = 2n + 1. \tag{4.79}$$

And the corresponding eigensolutions are the Hermite Gaussians,

$$\psi_n(\xi) = \text{const.}\ H_n(\xi)\ e^{-\frac{1}{2}\xi^2}, \tag{4.80}$$

which we discovered already as solutions of the paraxial wave equation, see Eqs.(2.298) and (2.299), i.e.

$$H_n(\xi) = (-1)^n e^{\xi^2}\ \frac{d^n}{d\xi^n}\ e^{-\xi^2} \tag{4.81}$$

$$\begin{array}{ll} H_0(\xi) = 1 \quad , & H_3(\xi) = 8\ \xi^3 - 12\ \xi \quad , \\ H_1(\xi) = 2\ \xi \quad , & H_4(\xi) = 16\ \xi^4 - 48\ \xi^2 + 12 \quad , \\ H_2(\xi) = 4\ \xi^2 - 2 \quad , & H_5(\xi) = 32\ \xi^5 - 160\ \xi^3 + 120\ \xi \quad . \end{array} \tag{4.82}$$

After denormalization and normalization the stationary wave functions are

$$\psi_n(x) = \sqrt{\frac{a}{2^n \sqrt{\pi}\ n!}}\ H_n(ax)\ e^{-\frac{1}{2}a^2x^2}. \tag{4.83}$$

Again, we find that the Hermite Gaussians constitute an orthogonal system of functions such that

$$\int_{-\infty}^{+\infty} \psi_m(x)^* \psi_n(x)\, dx = \delta_{mn}. \tag{4.84}$$

Figure 4.5 shows the first six stationary states or energy eigenstates of the harmonic oscillator.

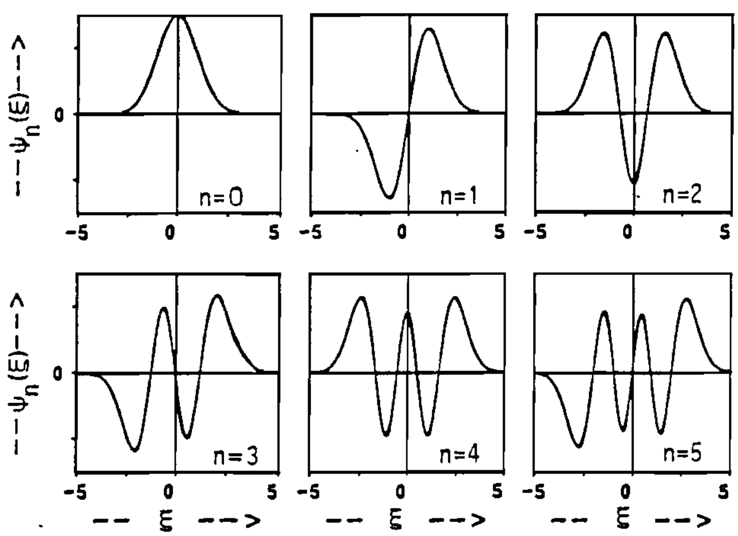

Figure 4.5: First six stationary states of the harmonic oscillators.

The energy eigenvalues of the stationary states are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_0\,. \tag{4.85}$$

Note, that the energy eigenvalues are equidistant and the difference between two energy eigenstates follows the findings of Planck. An oscillator has discrete energy levels which differ by energy quanta of size $\hbar\omega_0$, see Figure

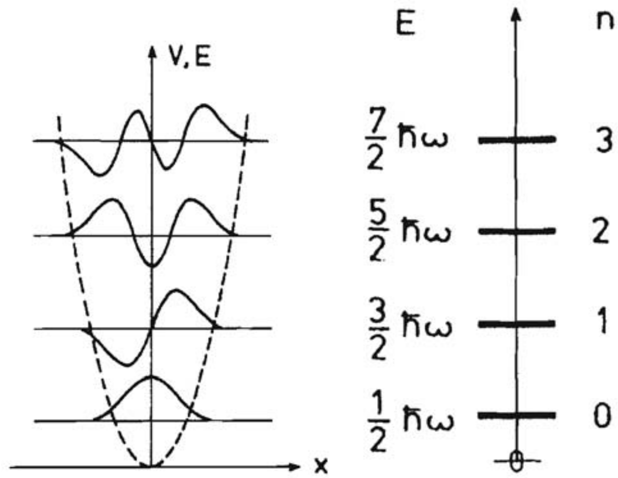

Figure 4.6: Lowest order wavefunctions of the harmonic oscillator and the corresponding energy eigenvalues [3].

.The only difference is, that the whole energy scale is shifted by the energy of half a quantum, which is the lowest energy eigenvalue. Thus the minimum energy, or ground state energy, of a harmonic oscillator is not zero but $E_0 = \frac{1}{2}\hbar\omega_0$.It is obvious, that an oscillator can not have zero energy because its energy is made up of kinetic and potential energy

$$E = \frac{p^2}{2m} + \frac{1}{2}\,Kx^2. \tag{4.86}$$

Since every state has to fulfill Heisenberg's uncertainty relation $\Delta p \cdot \Delta p \geq \frac{\hbar}{2}$, one can show that the state with minimum energy possible has an energy $E_0 = \frac{1}{2}\hbar\omega_0$, which is true for the ground state $\psi_0(x)$ according to Eq.(4.83). The stationary states of the harmonic oscillator correspond to states with precisely definied energy but completely undefined phase. If we assume a classical harmonic oscillator with a well defined energy $E = \frac{1}{2}\,Kx_0^2$. Note, that during a harmonic oscillation the energy is periodically converted from potential energy to kinetic energy. Then the oscillator oscillates with a fixed ampltiude x_0

$$x(t) = x_0 \cos(\omega_0 t + \varphi). \tag{4.87}$$

If the phase is assumed to be random in the interval [-π, π], one finds for the probability density of the position x to be

$$p(x) = \frac{1}{\pi\sqrt{x_0^2 - x^2}}.$$

Figure 4.7 shows this probability density corresponding to an energy eigenstate $\psi_n(x)$ with quantum large quantum number $n = 10$.

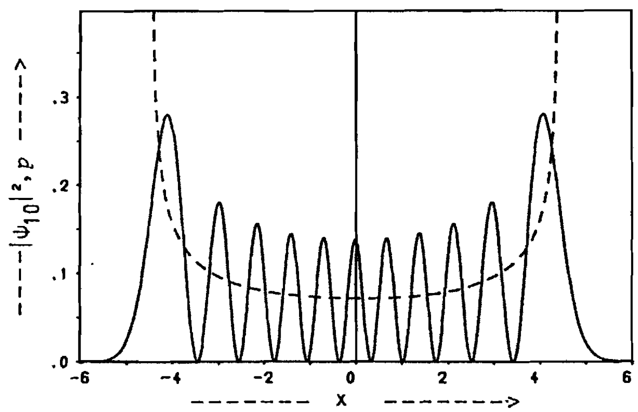

Figure 4.7: Probability density $|\psi_{10}|^2$ of the harmonic oscillator containing exactly 10 energy quanta.

On average, the quantum mechanical probability density agrees with the classical probability density, which is some form of the correspondence principle, which says that for large quantum numbers n the wave functions resume classical properties.

4.5 The Hydrogen Atom

The simplest of all atoms is the Hydrogen atom, which is made up of a positively charged proton with rest mass $m_p = 1.6726231 \times 10^{-27}$ kg, and a negatively charged electron with rest mass $m_e = 9.1093897 \times 10^{-31}$ kg. Therefore, the hydrogen atom is the only atom which consists of only two particles. This makes an analytical solution of both the classical as well as the quantum mechanical dynamics of the hydrogen atom possible. All other atomes are composed of a nucleus and more than one electron. According

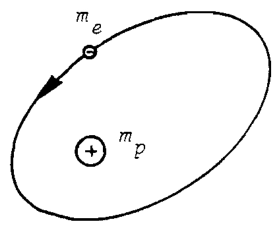

Figure 4.8: Bohr Sommerfeld model of the Hydrogen atom.

to the Bohr-Somerfeld model of hydrogen, the electron circles the proton on a planetary like orbit, see Figure 4.8.The stationary Schroedinger Equation for the Hydrogen atom is

$$\Delta\psi\left(\vec{r}\right)+\frac{2m_0}{\hbar^2}\left(E-V\left(\vec{r}\right)\right)\ \psi\left(\vec{r}\right)=0 \tag{4.88}$$

The potential is a Coulomb potential between the proton and the electron such that

$$V\left(\vec{r}\right)=-\frac{e_0^2}{4\,\pi\,\varepsilon_0\,\left|\vec{r}\right|} \tag{4.89}$$

and the mass is actually the reduced mass

$$m_0=\frac{m_p\ \cdot\ me}{m_p+m_e} \tag{4.90}$$

that arises when we transform the two body problem between electron and proton into a problem for the center of mass and relative coordinate motion. Due to the large, but finite, mass of the proton, i.e. the proton mass is 1836 times the electron mass, both bodies circle around a common center of mass. The center of mass is very close to the position of the proton and the reduced mass is almost identical to the proton mass. Due to the spherical symmetry of the potential the use of spherical coordinates is advantageous

$$\Delta\psi=\frac{\partial^2\psi}{\partial r^2}+\frac{2}{r}\,\frac{\partial\psi}{\partial r}+\frac{1}{r^2}\left[\frac{1}{\sin\vartheta}\,\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial\psi}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\,\frac{\partial^2\psi}{\partial\,\varphi^2}\right] \tag{4.91}$$

We will derive separate equations for the radial and angular coordinates by assuming trial solutions which are products of functions only depending on one of the coordinates r , ϑ , or φ

$$\psi\,(r, \vartheta, \varphi) = R\,(r) \quad \theta\,(\vartheta) \quad \phi\,(\varphi) \ . \tag{4.92}$$

Substituting this trial solution into the stationary Schroedinger Eq.(4.91) and separating variables leads to radial equation

$$\frac{d^2R}{dr^2} + \frac{2}{r}\,\frac{dR}{dr} + \left(\frac{2m_0E}{\hbar^2} + \frac{m_0e_0^2}{2\pi\varepsilon_0\hbar^2 r} - \frac{\alpha}{r^2}\right) R = 0 \quad , \tag{4.93}$$

the azimuthal equation

$$\frac{1}{\sin\vartheta}\,\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\theta}{d\vartheta}\right) + \left(\alpha - \frac{m^2}{\sin^2\vartheta}\right)\theta = 0 \quad , \tag{4.94}$$

and the polar equation

$$\frac{d^2\phi}{d\varphi^2} + m^2\phi = 0 \quad , \tag{4.95}$$

where α and m are constants yet to be determined. The polar equation has the complex solutions

$$\phi\,(\varphi) = \text{const.}\ e^{jm\varphi}, \ \text{with}\ m = \ldots - 2, -1, 0, 1, 2\ldots \tag{4.96}$$

because of the symmetry of the problem in the polar angle φ, i.e. the wave-function must be periodic in φ with period 2π.

4.5.1 Spherical Harmonics

The azimuthal equation is transformed by the substitution

$$\xi = \cos\vartheta \tag{4.97}$$

into

$$\left(1-\xi^2\right)\frac{d^2\theta}{d\xi^2} - 2\xi\frac{d\theta}{d\xi} + \left(\alpha - \frac{m^2}{1-\xi^2}\right)\theta = 0 \quad . \tag{4.98}$$

It turns out, that this equation has only bounded solutions on the interval $\xi\epsilon[-1, 1]$, if the constant α is a whole number

$$\alpha = l\,(l+1) \quad \text{with,} \quad l = 0, 1, 2\ldots \tag{4.99}$$

and

$$m = -l, -l+1, \ldots \quad -1, 0, 1 \ldots l-1, l \tag{4.100}$$

For $m = 0$, Eq.(4.98) is Legendre's Differential Equation and the solutions are the Legendre-Polynomialsm [5]

$$\begin{array}{ll} P_0(\xi) = 1\,, & P_3(\xi) = \frac{5}{2}\xi^3 - \frac{3}{2}\xi\,, \\ P_1(\xi) = \xi\,, & P_4(\xi) = \frac{35}{8}\xi^4 - \frac{15}{4}\xi^2 + \frac{3}{8}\,, \\ P_2(\xi) = \frac{3}{2}\xi^2 - \frac{1}{2}\,, & P_5(\xi) = \frac{63}{8}\xi^5 - \frac{35}{4}\xi^3 + \frac{15}{8}\xi\,. \end{array} \tag{4.101}$$

For $m \neq 0$, Eq.(4.98) is the associated Legendre's Differential Equation and the solutions are the associated Legendre-Polynomials, which can be generated from the Legendre-Polynomials by

$$P_1^m(\xi) = \left(1-\xi^2\right)^{m/2} \frac{d^m P_1(\xi)}{d\xi^m}. \tag{4.102}$$

Overall the angular functions can be combined to form the spherical harmonics

$$Y_1^m(\vartheta, \varphi) = (-1)^m \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\, P_1^m(\cos\vartheta)\, e^{\mathrm{j}m\,\varphi}\,, \tag{4.103}$$

which play an important role whenever a partial differential equation that contains the Laplace operator is solved in spherical coordinates. The spherical harmonics form a system of orthogonal functions on the full volume angle 4π, i.e. $\vartheta\epsilon[0, \pi]$ and $\varphi\epsilon[-\pi, \pi]$

$$\int_0^{\pi}\int_0^{2\pi} Y_l^{m*}(\vartheta, \varphi)\, Y_{l'}^{m'}(\vartheta, \varphi) \sin\vartheta \; d\vartheta \; d\varphi = \delta_{ll'}, \delta_{mm'}. \tag{4.104}$$

Therefore, a function of the angular variable (ϑ, φ) can be expanded in spherical harmonics. The spherical harmonics with negative azimuthal number -m can be expressed in terms of those with positive azimuthal number m.

$$Y_1^{-m}(\vartheta, \varphi) = (-1)^m \left(Y_l^m(\vartheta, \varphi)\right)^* \quad . \tag{4.105}$$

The lowest order spherical harmonics are listed in Table 4.1. Figure 4.9 shows a cut through the spherical harmonics $Y_1^m(\vartheta, \varphi)$ along the meridional plane.