

Lecture Notes on Quantum Mechanics

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Preface

These lecture notes summarize the main content of the course Quantum Mechanics I (Theory D), taught at the Karlsruhe Institute of Technology during the summer semester 2015. They are based on the graduate course Quantum Physics, taught at Iowa State University during Fall 2006, 2007 and 2008.

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Chapter 1

The Schrödinger equation

1.1 De Broglie's matter waves

The beginning of the 20th century was characterized by an increasing accumulation of experimental data that could not be understood anymore using classical mechanics, electrodynamics or classical statistical mechanics, even though these approaches proved highly successful for a broad range of problems. These developments include:

1898	Marja Sklodowska (Mdm. Curie)	Radioactive polonium and radium
1901	Max Planck	Unification of blackbody radiation
1905	Albert Einstein	Photoelectric effect
1911	Ernest Rutherford	Internal structure of the atom
1913	Niels Bohr	Quantum theory of spectra
1922	Compton	Scattering photons off electrons
1927	Davisson-Germer	electron interference measurement

These observations led to Planck's analysis of the black-body radiation and Einstein's postulate that light should be understood as a superposition of single quanta whose energy E and frequency ν are related by

$$E = h\nu. \quad (1.1)$$

The proportionality factor is Planck's constant

$$h = 6.6260755 \times 10^{-34} \text{Js} \quad (1.2)$$

and has dimension energy \times time, just like an action. In his 1900 publication Planck already estimates the value $h \simeq 6.55 \times 10^{-34} \text{Js}$. The momentum of the photon is

$$p = \frac{E}{c} = \frac{h\nu}{c}. \quad (1.3)$$

Using the wave length $\lambda = c/\nu$ and, what is often more convenient, the wave number

$$k = \frac{2\pi}{\lambda} \quad (1.4)$$

it then follows

$$p = \hbar k \quad (1.5)$$

with

$$\hbar = \frac{h}{2\pi} = 1.05457266 \times 10^{-34} \text{ Js.} \quad (1.6)$$

Similarly this yields

$$E = \hbar\omega \quad (1.7)$$

with angular frequency $\omega = 2\pi\nu$.

The idea that there is a particle character in what was accepted to be a wave had a complement in case of electrons. Those were believed to be particles, yet they displayed interference phenomena and thus behaves as waves. Louis de Broglie then made the radical assumption that not only photons have a particle-wave duality. The same is true for electrons and other quantum particles. He assumed similarly that there are waves obeying $p = \hbar k$ and $E = \hbar\omega$. However, the $\omega(k)$ dependence must be consistent with the energy momentum dispersion relation

$$E = \frac{p^2}{2m}. \quad (1.8)$$

It is said that Schrödinger only wanted to put the de Broglie relationship on a formally more satisfying level and searched for a wave equation that reproduces the proper dispersion relation. Let us try to guess how such a wave equation could look like. To obtain the correct dispersion relation we start from the equation:

$$a \frac{\partial^n \psi}{\partial t^n} = b \frac{\partial^m \psi}{\partial x^m}. \quad (1.9)$$

We want ψ to be a wave, i.e. a solution of the kind

$$\psi \propto \exp(ikx - i\omega t). \quad (1.10)$$

It holds $\frac{\partial^n \psi}{\partial t^n} = (-i)^n \omega^n \psi$ and $\frac{\partial^m \psi}{\partial x^m} = i^m k^m \psi$ and we find

$$a (-i)^n \omega^n \psi = b i^m k^m \psi. \quad (1.11)$$

Since we want our wave equation to yield

$$\omega = \frac{E}{\hbar} = \frac{p^2/(2m)}{\hbar} = \frac{\hbar k^2}{2m} \quad (1.12)$$

we can insert this and find

$$a (-i)^n \left(\frac{\hbar k^2}{2m} \right)^n = b i^m k^m \quad (1.13)$$

This requires a fixed relation between the temporal and spatial derivatives:

$$n = \frac{m}{2}. \quad (1.14)$$

The number of time derivatives is half the number of space derivatives. This result follows directly from the classical dispersion relation $E = \frac{p^2}{2m}$, where the energy is the square of momentum. In addition it holds for the pre-factors

$$a(-i)^n \left(\frac{\hbar}{2m} \right)^n = bi^m \quad (1.15)$$

This only determines (for given n) the ratio a/b . The simplest choice (but by no means a unique choice) is to start with $n = 1$. This leads with $a = i\hbar$ to:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}. \quad (1.16)$$

This is the Schrödinger equation for a single non-interacting non-relativistic particle.

1.2 Interpretation of the Schrödinger equation

The generalization of the Schrödinger equation to more than one spatial dimension is obvious:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi. \quad (1.17)$$

Having arrived at this new equation of motion a number of questions arise:

1. What is the physical interpretation of $\psi(x, t)$?
2. How to go beyond the limit of a particle on free space, i.e. how does this equation look like in case of a finite potential?
3. How can one make contact to Newton's equation of motion that proved to be so successful for the mechanical motion of macroscopic bodies?

etc. etc.

A proposal that addresses the first question was made very early on by Max Born. He realized that $\psi(\mathbf{x}, t)$ has not only an arbitrary sign (after all it is a wave). In general it can also be complex. The latter is due to the fact that time and space derivatives enter differently, leading to the imaginary unit i in the wave equation. It makes therefore no sense to talk about a large or a small wave function $\psi(\mathbf{x}, t)$. On the other hand $|\psi(\mathbf{x}, t)|^2$ can be large or small. Since it is positive definite it seems natural to call $|\psi(\mathbf{x}, t)|^2$ the density of the quantum particle. However, since the wave function is supposed to describe the properties of individual elementary particles, it makes strictly no sense to call $|\psi(\mathbf{x}, t)|^2$ the particle density, a notion that requires that some fraction of the particle is

located at one position and another fraction elsewhere. Born refined this and called

$$\rho(\mathbf{r}, t) = |\psi(\mathbf{x}, t)|^2 = \psi^*(\mathbf{x}, t) \psi(\mathbf{x}, t) \quad (1.18)$$

the probability density. Thus, knowing $|\psi(\mathbf{x}, t)|^2$ determines the probability to find the electron at a given time, t , at position \mathbf{x} . This makes of course only sense if the probability distribution is properly normalized, i.e. that:

$$\int d^3r \rho(\mathbf{r}, t) = \int d^3x \psi^*(\mathbf{x}, t) \psi(\mathbf{x}, t) = 1. \quad (1.19)$$

Since the Schrödinger equation is a linear equation it holds that $\lambda\psi(\mathbf{x}, t)$ is a solution if $\psi(\mathbf{x}, t)$ is a solution, where λ is a time and coordinate independent complex number. Thus, we can always fix λ to ensure Eq.1.19.

From probability we know that the expectation value of \mathbf{x} , (i.e. the mean value of the position) is given by

$$\begin{aligned} \langle \mathbf{x} \rangle_t &= \int d^3x \mathbf{x} \rho(\mathbf{x}, t) \\ &= \int d^3x \psi^*(\mathbf{x}, t) \mathbf{x} \psi(\mathbf{x}, t). \end{aligned} \quad (1.20)$$

Similarly, the mean square of the position is

$$\begin{aligned} \langle \mathbf{x}^2 \rangle_t &= \int d^3x \mathbf{x}^2 \rho(\mathbf{x}, t) \\ &= \int d^3x \psi^*(\mathbf{x}, t) \mathbf{x}^2 \psi(\mathbf{x}, t). \end{aligned} \quad (1.21)$$

The velocity (i.e. the change of the mean particle with time) is then

$$\begin{aligned} \langle \mathbf{v} \rangle_t &= \frac{\partial}{\partial t} \langle \mathbf{x} \rangle_t \\ &= \int d^3x \left(\frac{\partial}{\partial t} \psi^*(\mathbf{x}, t) \right) \mathbf{x} \psi(\mathbf{x}, t) + \int d^3x \psi^*(\mathbf{x}, t) \mathbf{x} \frac{\partial}{\partial t} \psi(\mathbf{x}, t) \\ &= \frac{\hbar}{2mi} \int d^3x [(\nabla^2 \psi^*) \mathbf{x} \psi(\mathbf{x}, t) - \psi^*(\mathbf{x}, t) \mathbf{x} \nabla^2 \psi(\mathbf{x}, t)] \\ &= \frac{\hbar}{2mi} \int d^3x [\psi^* \nabla^2 \mathbf{x} \psi(\mathbf{x}, t) - \psi^*(\mathbf{x}, t) \mathbf{x} \nabla^2 \psi(\mathbf{x}, t)] \\ &= \frac{\hbar}{2mi} \int d^3x [\psi^* \nabla \cdot ((\nabla \mathbf{x}) \psi(\mathbf{x}, t) + \mathbf{x} \nabla \psi(\mathbf{x}, t)) - \psi^*(\mathbf{x}, t) \mathbf{x} \nabla^2 \psi(\mathbf{x}, t)] \\ &= \frac{\hbar}{2mi} \int d^3x [\psi^* ((\nabla \mathbf{x}) \cdot \nabla \psi(\mathbf{x}, t) + (\nabla \mathbf{x}) \cdot \nabla \psi(\mathbf{x}, t) + \mathbf{x} \nabla^2 \psi(\mathbf{x}, t)) \\ &\quad - \psi^*(\mathbf{x}, t) \mathbf{x} \nabla^2 \psi(\mathbf{x}, t)] \\ &= \frac{\hbar}{mi} \int d^3x \psi^*(\mathbf{x}, t) \nabla \psi(\mathbf{x}, t) = \frac{1}{m} \left\langle \frac{\hbar}{i} \nabla \right\rangle_t \end{aligned}$$

Classically we would expect that

$$\langle \mathbf{v} \rangle_t = \frac{1}{m} \langle \mathbf{p} \rangle_t \quad (1.22)$$

and we therefore realize that in order to determine the mean value of the momentum we have to evaluate the average of

$$\hat{\mathbf{p}} = \frac{\hbar}{i} \nabla \quad (1.23)$$

The physical quantity momentum is therefore represented by the operator $\frac{\hbar}{i} \nabla$. This makes a lot of sense as

$$\hat{\mathbf{p}} \exp(i\mathbf{k} \cdot \mathbf{x} - i\omega t) = \hbar \mathbf{k} \exp(i\mathbf{k} \cdot \mathbf{x} - i\omega t). \quad (1.24)$$

For a perfect plane wave is the application of the operator $\hat{\mathbf{p}}$ identical to the simple multiplication with $\hbar \mathbf{k}$, the momentum according to the de Broglie prescription. If correct, it suggests that the kinetic energy is represented by the operator

$$\hat{T} = \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} = -\frac{\hbar^2}{2m} \nabla^2, \quad (1.25)$$

i.e. the Schrödinger equation for the free particle can be written as

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{T} \psi, \quad (1.26)$$

suggesting that in case of a finite potential $V(\mathbf{x})$ the Schrödinger equation reads

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi, \quad (1.27)$$

where

$$\hat{H} = \hat{T} + \hat{V} \quad (1.28)$$

is the energy operator. More precisely it is the *Hamilton operator*. $\hat{V} = V(\hat{\mathbf{x}})$ is an operator, where the operator $\hat{\mathbf{x}}$ is defined as

$$\hat{\mathbf{x}} \psi(\mathbf{x}, t) = \mathbf{x} \psi(\mathbf{x}, t), \quad (1.29)$$

consistent with our above usage. This addresses question 2 above.

Eq.1.27 allows us to analyze the time dependence of an arbitrary expectation value of an operator \hat{A}

$$\langle \hat{A} \rangle_t = \int d^3x \psi^*(\mathbf{x}, t) \hat{A} \psi(\mathbf{x}, t). \quad (1.30)$$

It follows

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \langle \hat{A} \rangle_t &= - \int d^3x \left(\hat{H} \psi^*(\mathbf{x}, t) \right) \hat{A} \psi(\mathbf{x}, t) - \psi^*(\mathbf{x}, t) \hat{A} \hat{H} \psi(\mathbf{x}, t) \\ &= - \int d^3x \psi^*(\mathbf{x}, t) \hat{H} \hat{A} \psi(\mathbf{x}, t) - \psi^*(\mathbf{x}, t) \hat{A} \hat{H} \psi(\mathbf{x}, t) \\ &= \left\langle \left[\hat{A}, \hat{H} \right] \right\rangle_t, \end{aligned} \quad (1.31)$$

where we introduced the commutator

$$[\hat{A}, \hat{H}] = \hat{A}\hat{H} - \hat{H}\hat{A}. \quad (1.32)$$

Eq.1.31 is called the Ehrenfest theorem.

The commutator determines to what extend the order of the application of two operators matters. To evaluate commutators it is best to apply it to a wave function. For example:

$$\begin{aligned} [\hat{p}_\alpha, \hat{x}_\beta] \psi &= \frac{\hbar}{i} \frac{\partial}{\partial x_\alpha} (x_\beta \psi) - x_\beta \frac{\hbar}{i} \frac{\partial}{\partial x_\alpha} \psi \\ &= \frac{\hbar}{i} \left(\frac{\partial}{\partial x_\alpha} x_\beta \right) \psi + \frac{\hbar}{i} x_\beta \frac{\partial}{\partial x_\alpha} \psi - x_\beta \frac{\hbar}{i} \frac{\partial}{\partial x_\alpha} \psi \\ &= \frac{\hbar}{i} \delta_{\alpha\beta} \psi \end{aligned} \quad (1.33)$$

It follows for the operators:

$$[\hat{p}_\alpha, \hat{x}_\beta] = \frac{\hbar}{i} \delta_{\alpha\beta}. \quad (1.34)$$

This yields

$$\begin{aligned} [\hat{\mathbf{p}}^2, \hat{x}_\alpha] &= \sum_\beta (\hat{p}_\beta \hat{p}_\beta \hat{x}_\alpha - \hat{x}_\alpha \hat{p}_\beta \hat{p}_\beta) \\ &= \sum_\beta \left(\hat{p}_\beta \hat{x}_\alpha \hat{p}_\beta - \hat{x}_\alpha \hat{p}_\beta \hat{p}_\beta + \frac{\hbar}{i} \delta_{\alpha\beta} \hat{p}_\beta \right) \\ &= -i2\hbar \hat{p}_\alpha \end{aligned} \quad (1.35)$$

and we obtain again our earlier result

$$\begin{aligned} \frac{\partial}{\partial t} \langle \hat{\mathbf{x}} \rangle_t &= \frac{i}{\hbar} \langle [\hat{H}, \hat{\mathbf{x}}] \rangle_t \\ &= \frac{i}{\hbar 2m} \langle [\hat{\mathbf{p}}^2, \hat{\mathbf{x}}] \rangle_t = \frac{1}{m} \langle \hat{\mathbf{p}} \rangle_t \end{aligned} \quad (1.36)$$

Similarly we can analyze

$$\frac{\partial}{\partial t} \langle \hat{\mathbf{p}} \rangle_t = \frac{i}{\hbar} \langle [\hat{H}, \hat{\mathbf{p}}] \rangle_t = \frac{i}{\hbar} \langle [\hat{V}, \hat{\mathbf{p}}] \rangle_t \quad (1.37)$$

It holds

$$\begin{aligned} V(\mathbf{x}) \hat{p}_\alpha \psi - \hat{p}_\alpha V(\mathbf{x}) \psi &= V(\mathbf{x}) \frac{\hbar}{i} \frac{\partial}{\partial x_\alpha} \psi - \frac{\hbar}{i} \frac{\partial}{\partial x_\alpha} (V(\mathbf{x}) \psi) \\ &= -\frac{\hbar}{i} \left(\frac{\partial}{\partial x_\alpha} V(\mathbf{x}) \right) \psi \end{aligned} \quad (1.38)$$

and we obtain

$$\frac{\partial}{\partial t} \langle \hat{\mathbf{p}} \rangle_t = -\langle \nabla V(\mathbf{x}) \rangle_t. \quad (1.39)$$

This is indeed identical similar to Newton's equation of motion, since

$$\mathbf{F}(\mathbf{x}) = -\nabla V(\mathbf{x}) \quad (1.40)$$

is nothing but the classical force. The change of the averaged momentum is given by the averaged force. This relation between $\frac{\partial}{\partial t} \langle \hat{\mathbf{p}} \rangle_t$ and $\langle \mathbf{F} \rangle$ is called the Ehrenfest theorem. All the beauty of quantum mechanics is apparently hidden in the deviations from mean values. Still, in case of very narrow distribution functions we see that there seems to exist a natural relation to the classical limit. Thus we have answered question 2 above in the sense that classical physics was so far concerned with the properties of mean values, while there are deviations from the mean values, so called quantum fluctuations, that are due to the wave nature of quantum particles.

1.3 Stationary Schrödinger equation

In case of an arbitrary time-independent potential, the Schrödinger equation can be simplified. We make the product ansatz¹

$$\psi(\mathbf{x}, t) = f(t) \psi(\mathbf{x}), \quad (1.41)$$

which gives

$$i\hbar \frac{\partial f(t)}{\partial t} \psi(\mathbf{x}) = -\frac{\hbar^2}{2m} f(t) \nabla^2 \psi(\mathbf{x}) + f(t) V(\mathbf{x}) \psi(\mathbf{x}) \quad (1.42)$$

and we obtain

$$\frac{i\hbar \frac{\partial f(t)}{\partial t}}{f(t)} = \frac{-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{x}) + V(\mathbf{x}) \psi(\mathbf{x})}{\psi(\mathbf{x})}. \quad (1.43)$$

Since a purely time dependent function on the l.h.s. equals a purely space dependent function on the r.h.s., both can only be a constant

$$\begin{aligned} i\hbar \frac{\partial f(t)}{\partial t} &= E f(t) \\ \hat{H} \psi(\mathbf{x}) &= E \psi(\mathbf{x}) \end{aligned} \quad (1.44)$$

The first equation is solved readily:

$$f(t) = f(0) e^{-i\frac{E}{\hbar}t}. \quad (1.45)$$

The time dependence of the wave function is then only a phase factor. In case of time-independent potentials, the probability distribution $|\psi(x, t)|^2 = |\psi(x)|^2$ is independent on t .

The second equation is the time independent or stationary Schrödinger equation. It is an eigenvalue equation. In order to interpret the constant E we realize

¹We use the common but slightly misleading notation where $\psi(x, t)$ refers to the full space and time dependent wave function and $\psi(x)$ to the space dependent part of it.

that it is the *eigenvalue* of the Hamilton operator. For the expectation value of the Hamilton operator follows:

$$\begin{aligned}\langle \hat{H} \rangle &= \int dx \psi^*(x, t) \hat{H} \psi(x, t) \\ &= E \int dx \psi^*(x, t) \psi(x, t) = E\end{aligned}\quad (1.46)$$

i.e. E is the expectation value of the energy in the state $\psi(x, t)$. Thus, if a quantum mechanical system is characterized by an eigenfunction of the Hamilton operator, its energy is sharply defined and given by the associated eigenvalue.

1.4 Particle in a box

In order to get a better impression for the transition from the quantum to the classical world we consider a simple example, the one dimensional potential well. We consider a particle in one dimension (i.e. moving on a thin wire) that is confined to move in the interval $[-\frac{a}{2}, \frac{a}{2}]$. The corresponding potential is

$$V(x) = \begin{cases} 0 & |x| < \frac{a}{2} \\ \infty & |x| \geq \frac{a}{2} \end{cases} . \quad (1.47)$$

Classically the motion of a particle on this wire is

$$x(t) = x_0 + vt, \quad (1.48)$$

at least until it is reflected on the walls. The probability of finding the particle in the interval $[x, x + dx]$ under the condition that x_0 is unknown equals the fraction of time it spends in this interval. Thus

$$\rho_{\text{class}} dx = \frac{v dt}{a} = \frac{dx}{a} \quad (1.49)$$

yielding the obvious result that

$$\rho_{\text{class}} = \frac{1}{a} = \text{const.} \quad (1.50)$$

Since our potential is time-independent we can immediately focus on the stationary Schrödinger equation

$$\hat{H}\psi(\mathbf{x}) = E\psi(\mathbf{x}). \quad (1.51)$$

The infinite potential is only compatible with a vanishing wave function, i.e. we need to request $\psi(|x| \geq \frac{a}{2}) = 0$. Inside the well the potential vanishes and it holds

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = E\psi(x). \quad (1.52)$$

As discussed, the total, time-dependent wave function is given as:

$$\psi(x, t) = e^{-i\frac{E}{\hbar}t}\psi(x) \quad (1.53)$$

We further introduce for convenience the quantity k via

$$E = \frac{\hbar^2}{2m}k^2 \quad (1.54)$$

and obtain

$$\frac{\partial^2}{\partial x^2}\psi(x) + k^2\psi(x) = 0. \quad (1.55)$$

The solutions of this second order differential equation with constant coefficients is well known as:

$$\psi(x) = A \cos(kx) + B \sin(kx). \quad (1.56)$$

The two boundary conditions are

$$\begin{aligned} \psi\left(\frac{a}{2}\right) &= A \cos(ka/2) + B \sin(ka/2) = 0 \\ \psi\left(-\frac{a}{2}\right) &= A \cos(ka/2) - B \sin(ka/2) = 0, \end{aligned} \quad (1.57)$$

which gives

$$\begin{aligned} A \cos(ka/2) &= 0 \\ B \sin(ka/2) &= 0. \end{aligned} \quad (1.58)$$

Thus, it must hold $A = 0$ or $k = (2m + 1)\frac{\pi}{a}$ as well as $B = 0$ or $k = 2m\frac{\pi}{a}$. Thus, using

$$k_n = n\frac{\pi}{a} \quad (1.59)$$

$$\psi(x) = \begin{cases} \sqrt{\frac{2}{a}} \cos(k_n x) & n \text{ odd} \\ \sqrt{\frac{2}{a}} \sin(k_n x) & n \text{ even} \end{cases} \quad (1.60)$$

The application of the kinetic energy equals the multiplication of the wave function with the eigenvalue

$$E_n = \frac{\hbar^2}{2m}k_n^2 = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2} n^2 \quad (1.61)$$

Only a discrete set of energies is allowed. Energy is quantized!

Obviously we need to exclude $n = 0$ as it corresponds to $\psi(x) = 0$ which is not normalizable. The lowest energy is therefore

$$E_1 = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2}. \quad (1.62)$$

Even though the potential vanishes in the box (and classically a particle at rest with energy $E = 0$ is allowed) this is not the case for the quantum solutions. There exists a rather transparent physical interpretation for this *zero-point energy* effect: In order to squeeze a wave in the box with proper boundary conditions we need a wave length

$$\lambda = \frac{a}{2} \quad (1.63)$$

yielding a wave number

$$k = \frac{2\pi}{\lambda} = \frac{\pi}{a} \quad (1.64)$$

which yields a energy

$$E = E_1 = \frac{\hbar^2 \pi^2}{2m a^2}. \quad (1.65)$$

The wave nature of the solution simply enforces a finite kinetic energy of the solution.

We also observe that we have two classes of solution that alternate if we order them by their energy. Solutions with n odd are even under reflection

$$\psi_n(x) = \psi_n(-x) \quad (1.66)$$

while the other solutions change sign

$$\psi_n(x) = -\psi_n(-x). \quad (1.67)$$

Thus while the potential is always even under reflection $x \rightarrow -x$, the wave function does not need to have this symmetry property. More generally: the symmetry of the wave function can be lower than that of the Hamiltonian.

Finally, we analyze the probability density $|\psi_n(x)|^2 = \frac{2}{a} \cos^2(n\pi x/a)$ or $|\psi_n(x)|^2 = \frac{2}{a} \sin^2(n\pi x/a)$. For large enough n this oscillates rapidly around the classical value $\rho_{\text{class}} = \frac{1}{a}$. Averaging over regions of size $\delta x \simeq a/n$ (that are small compared to a for large n) gives:

$$\int_{x, x+\delta x} dx |\psi_n(x)|^2 \rightarrow \rho_{\text{class}}. \quad (1.68)$$

In this sense is it possible to recover the classical limit. While states with low energy behave fundamentally different from the classical limit, highly excited states with large energy become increasingly similar to the behavior obtained within classical mechanics. While the statement that mean values follows the classical equations of motion is generally correct, the deviations from the mean values are significant for low energy states.

This can also be seen from an analysis of the mean square deviation $\langle x^2 \rangle$: It holds

$$\langle x \rangle = \int_{-a/2}^{a/2} x |\psi(x)|^2 dx = 0, \quad (1.69)$$

as $|\psi(x)|^2$ is always an even function, making the above integrand an odd function. On the average the particle is always in the middle. However it follows easily (see Mathematica analysis)

$$\langle x^2 \rangle = \int_{-a/2}^{a/2} x^2 |\psi(x)|^2 dx = \frac{a^2}{12} \left(1 - \frac{6}{n^2 \pi^2} \right). \quad (1.70)$$

Thus, highly excited states have mean square deviations that approach $\langle x^2 \rangle \rightarrow \frac{a^2}{12}$. This is exactly what we expect classically

$$\begin{aligned} \langle x^2 \rangle &= \int_{-a/2}^{a/2} \rho_{\text{class}} x^2 dx = \frac{1}{a} \int_{-a/2}^{a/2} x^2 dx \\ &= \frac{1}{3a} x^3 \Big|_{-a/2}^{a/2} = \frac{a^2}{12}. \end{aligned} \quad (1.71)$$

1.5 Continuity of probability

We interpreted

$$\rho(\mathbf{x}, t) = |\psi(\mathbf{x}, t)|^2 \quad (1.72)$$

as probability density. It is therefore natural to ask whether probability is conserved. Charge conservation in electrodynamics is for example related to the conservation law

$$\frac{\partial}{\partial t} \rho(\mathbf{x}, t) + \nabla \cdot \mathbf{j}(\mathbf{x}, t) = 0 \quad (1.73)$$

with charge current $\mathbf{j}(\mathbf{x}, t)$. What is the corresponding expression for the probability current that follows from the Schrödinger equation.

It holds

$$\frac{\partial}{\partial t} \rho(\mathbf{x}, t) = \left(\frac{\partial}{\partial t} \psi(\mathbf{x}, t)^* \right) \psi(\mathbf{x}, t) + \psi(\mathbf{x}, t)^* \frac{\partial}{\partial t} \psi(\mathbf{x}, t) \quad (1.74)$$

We use the Schrödinger equation to determine the time dependence of ψ^* and ψ :

$$\begin{aligned} i\hbar \frac{\partial \psi}{\partial t} &= \hat{H} \psi \\ -i\hbar \frac{\partial \psi^*}{\partial t} &= \hat{H} \psi^*, \end{aligned} \quad (1.75)$$

which gives

$$\begin{aligned} \frac{\partial}{\partial t} \rho &= \left(-\frac{1}{i\hbar} \hat{H} \psi^* \right) \psi + \psi^* \frac{1}{i\hbar} \hat{H} \psi \\ &= \frac{\hbar}{2im} (\nabla^2 \psi^*) \psi - \psi^* \nabla^2 \psi \\ &= -\frac{\hbar}{2im} \nabla \cdot [\psi^* \nabla \psi - (\nabla \psi^*) \psi] \end{aligned} \quad (1.76)$$

Thus, the probability current is

$$\mathbf{j} = \frac{\hbar}{2im} (\psi^* \nabla \psi - (\nabla \psi^*) \psi). \quad (1.77)$$

The net current I through the surface, ∂V , of a given volume V is given by the change in the probability

$$P = \int_V d^3x \rho(\mathbf{x}, t)$$

in that volume:

$$\begin{aligned} \frac{\partial}{\partial t} P &= - \int_V d^3x \nabla \cdot \mathbf{j}(\mathbf{x}, t) \\ &= - \int_{\partial V} d\sigma \cdot \mathbf{j}(\mathbf{x}, t) = -I \end{aligned} \quad (1.78)$$

Here $d\sigma$ is the surface element with direction parallel to the surface normal vector. $I > 0$ means that the current flows out of the volume implying that P decreases.

Since we only talk about the absolute magnitude $|\psi(\mathbf{x}, t)|^2$ of the wave function one might think that the phase of the wave function carries no physical information. However, this is not the case. Lets write

$$\psi(\mathbf{x}, t) = \sqrt{\rho(\mathbf{x}, t)} \exp\left(\frac{iS(\mathbf{x}, t)}{\hbar}\right) \quad (1.79)$$

It then follows

$$\mathbf{j}(\mathbf{x}, t) = \frac{\rho(\mathbf{x}, t)}{m} \nabla S(\mathbf{x}, t) \quad (1.80)$$

The gradient of the phase determines the current flow of the probability and (except for an overall constant that doesn't contribute to the current) carries important information. Only a constant in space phase carries no physical information. This is obvious from the simple fact that $\psi(\mathbf{x}, t)$ solves the Schroedinger equation of $\psi(\mathbf{x}, t) e^{iS_0}$ does, where S_0 is independent on \mathbf{x} and t .

Chapter 2

Measurement and uncertainty

2.1 Hermitian operators

A crucial observation of our analysis so far was, that the physical quantities position $\hat{\mathbf{x}}$, momentum $\hat{\mathbf{p}}$ and energy \hat{H} are all represented by operators. We expect of course that their expectation values are real. This is obvious in case of the position operator

$$\langle \hat{\mathbf{x}} \rangle = \int d^3x \mathbf{x} |\psi(\mathbf{x}, t)|^2. \quad (2.1)$$

However, this is less obvious for $\hat{\mathbf{p}}$

$$\langle \hat{\mathbf{p}} \rangle = \frac{\hbar}{i} \int d^3x \psi^*(\mathbf{x}, t) \nabla \psi(\mathbf{x}, t). \quad (2.2)$$

Consider

$$\langle \hat{\mathbf{p}} \rangle^* = -\frac{\hbar}{i} \int d^3x \psi(\mathbf{x}, t) \nabla \psi^*(\mathbf{x}, t) \quad (2.3)$$

we find

$$\langle \hat{\mathbf{p}} \rangle - \langle \hat{\mathbf{p}} \rangle^* = \frac{\hbar}{i} \int d^3x \nabla |\psi(\mathbf{x}, t)|^2 \quad (2.4)$$

Using Gauss theorem this corresponds to $\frac{\hbar}{i} |\psi(\mathbf{x}, t)|^2$ taken on the surface of the integration volume. Formally one should always confine one selves to a specific set of permissible functions. Since we always want to reach normalizability

$$\int d^3x \psi^*(\mathbf{x}, t) \psi(\mathbf{x}, t) = 1 \quad (2.5)$$

it is obvious that the wave function must decay sufficiently fast for large x . Thus, the above surface term can always be safely neglected since $|\psi(\mathbf{x}, t)|^2$

vanishes at infinity. It follows that the expectation value of the momentum is indeed real. As an aside we also learned that quantum mechanics is described by the space of square integrable functions.

In case of the energy it also follows that

$$\langle H \rangle = \langle T \rangle + \langle V \rangle \quad (2.6)$$

is real. This is obvious in case of the potential energy:

$$\langle V \rangle = \int d^3x V(\mathbf{x}) |\psi(\mathbf{x}, t)|^2. \quad (2.7)$$

In case of the kinetic energy follows

$$\langle T \rangle = -\frac{\hbar^2}{2m} \int d^3x \psi(\mathbf{x}, t) \nabla^2 \psi^*(\mathbf{x}, t) \quad (2.8)$$

while

$$\begin{aligned} \langle T \rangle^* &= -\frac{\hbar^2}{2m} \int d^3x \psi^*(\mathbf{x}, t) \nabla^2 \psi(\mathbf{x}, t) \\ &= -\frac{\hbar^2}{2m} \int d^3x (\nabla^2 \psi^*(\mathbf{x}, t)) \psi(\mathbf{x}, t) \\ &= \langle T \rangle. \end{aligned} \quad (2.9)$$

Once again we performed partial integrations and neglected surface terms.

More generally we can say that physical quantities are represented by operators with real expectation values. Lets consider such a physical quantity, characterized by an operator \hat{O} . Consider the eigenfunctions of \hat{O}

$$\hat{O}\varphi_n = o_n\varphi_n. \quad (2.10)$$

For the expectation value to be real in general, all eigenvalues must be real. This is accomplished if we assume that \hat{O} is Hermitian, i.e. that

$$\int d^3x \psi^*(\mathbf{x}) \hat{O}\psi(\mathbf{x}) = \int d^3x (\hat{O}\psi(\mathbf{x}))^* \psi(\mathbf{x}). \quad (2.11)$$

In other words, it doesn't matter whether the operator acts on $\psi(\mathbf{x})$ or $\psi^*(\mathbf{x})$. Lets check that the eigenvalues of an Hermitian operator are real. It holds

$$\int d^3x \varphi_n^*(\mathbf{x}) \hat{O}\varphi_n(\mathbf{x}) = o_n \int d^3x \varphi_n^*(\mathbf{x}) \varphi_n(\mathbf{x}) \quad (2.12)$$

Lets take the complex conjugate

$$\int d^3x \varphi_n(\mathbf{x}) (\hat{O}\varphi_n(\mathbf{x}))^* = o_n^* \int d^3x \varphi_n^*(\mathbf{x}) \varphi_n(\mathbf{x}) \quad (2.13)$$

Thus $o_n^* = o_n$ for an Hermitian operator. It also follows easily that two eigenfunctions φ_n and φ_m with distinct eigenvalues o_n and o_m are orthogonal. It holds

$$\begin{aligned}\widehat{O}\varphi_n &= o_n\varphi_n \\ \widehat{O}\varphi_m &= o_m\varphi_m\end{aligned}\quad (2.14)$$

and it follows

$$\begin{aligned}\int d^3x\varphi_m^*(\mathbf{x})\widehat{O}\varphi_n(\mathbf{x}) &= o_n\int d^3x\varphi_m^*(\mathbf{x})\varphi_n(\mathbf{x}) \\ \int d^3x\varphi_n^*(\mathbf{x})\widehat{O}\varphi_m(\mathbf{x}) &= o_m\int d^3x\varphi_n^*(\mathbf{x})\varphi_m(\mathbf{x})\end{aligned}\quad (2.15)$$

Subtracting the first from the complex conjugate of the second equation gives

$$0 = (o_n - o_m)\int d^3x\varphi_m^*(\mathbf{x})\varphi_n(\mathbf{x}).\quad (2.16)$$

Thus, for distinct eigenvalues follows $\int d^3r\varphi_m^*(\mathbf{x})\varphi_n(\mathbf{x}) = 0$. If the eigenvalues are the same, we can always orthogonalize the eigenfunctions. Thus, one can always assume that the functions are orthonormal, i.e.

$$\int d^3x\varphi_n^*\varphi_m = \delta_{nm}.\quad (2.17)$$

An arbitrary function $\psi(\mathbf{x})$ can be written as superposition of the φ_n

$$\psi = \sum_n a_n\varphi_n.\quad (2.18)$$

We say that the $\{\varphi_n\}$ form a complete set of functions. The fact that the set of functions is complete follows from the relation

$$\sum_n \varphi_n^*(\mathbf{x})\varphi_n(\mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}')\quad (2.19)$$

If we want to calculate the expectation value of \widehat{O} , it follows:

$$\begin{aligned}\langle\widehat{O}\rangle &= \int d^3x\psi^*(\mathbf{x})\widehat{O}\psi(\mathbf{x}) \\ &= \sum_{n,m} a_n^*a_m\int d^3x\varphi_n^*\widehat{O}\varphi_m \\ &= \sum_n |a_n|^2 o_n.\end{aligned}\quad (2.20)$$

How can we determine the expansion coefficients a_n in $\psi = \sum_n a_n\varphi_n$? To determine them we multiply both sides of the equation by φ_m^* and integrate over space

$$\int d^3r\varphi_m^*(x)\psi(x) = \sum_n a_n\int d^3r\varphi_m^*(x)\varphi_n(x)\quad (2.21)$$

Now we use the ortho-normality $\int d^3r \varphi_m^*(x) \varphi_n(x) = \delta_{nm}$ and obtain

$$a_m = \int d^3r \varphi_m^*(x) \psi(x). \quad (2.22)$$

It follows

$$\begin{aligned} \sum_n |a_n|^2 &= \sum_n \int d^3x \int d^3x' \psi^*(\mathbf{x}) \varphi_n(\mathbf{x}) \psi(\mathbf{x}') \varphi_n^*(\mathbf{x}') \\ &= \int d^3x \psi^*(\mathbf{x}) \widehat{C} \psi(\mathbf{x}) \end{aligned} \quad (2.23)$$

where the action of the operator \widehat{C} is defined as

$$\widehat{C} \psi(\mathbf{x}) = \sum_n \int d^3x' \varphi_n(\mathbf{x}) \varphi_n^*(\mathbf{x}') \psi(\mathbf{x}') \quad (2.24)$$

$$= \sum_n a_n \varphi_n(\mathbf{x}) = \psi(\mathbf{x}) \quad (2.25)$$

such that $\widehat{C} = 1$ yielding

$$\sum_n |a_n|^2 = 1 \quad (2.26)$$

as expected for a probability distribution.

The above derived expression

$$\langle \widehat{O} \rangle = \sum_n |a_n|^2 o_n \quad (2.27)$$

has a nice physical interpretation. We can obviously interpret $|a_n|^2$ as the probabilities that o_n is in state n .

Let us finally comment on the completeness relation. Take an arbitrary function $\psi(\mathbf{x})$ and write

$$\begin{aligned} \psi(\mathbf{x}) &= \int d^d x' \delta(\mathbf{x} - \mathbf{x}') \psi(\mathbf{x}') \\ &= \sum_n \int d^d x' \varphi_n^*(\mathbf{x}) \varphi_n(\mathbf{x}') \psi(\mathbf{x}') \\ &= \sum_n a_n \varphi_n(\mathbf{x}), \end{aligned}$$

i.e. an arbitrary function can be represented in terms of the above expansion.

If we want to analyze the properties of an observable, i.e. a quantity that is characterized by a Hermitian operator \widehat{O} , it is interesting to investigate the deviations from the mean value.

$$\Delta \widehat{O} = \widehat{O} - \langle \widehat{O} \rangle \quad (2.28)$$

and consider the mean square deviation

$$\begin{aligned}
\left\langle (\Delta\hat{O})^2 \right\rangle &= \int d^d x \psi(\mathbf{x})^* \Delta\hat{O}\Delta\hat{O}\psi(\mathbf{x}) \\
&= \int d^d x (\Delta\hat{O}\psi(\mathbf{x}))^* \Delta\hat{O}\psi(\mathbf{x}) \\
&= \int d^d x |\Delta\hat{O}\psi(\mathbf{x})|^2
\end{aligned} \tag{2.29}$$

If O is a physical quantity that we can sharply determine in the state $\psi(\mathbf{x})$, it must hold $\left\langle (\Delta\hat{O})^2 \right\rangle = 0$. Since the integrand is positive definite, this can only hold for

$$\Delta\hat{O}\psi(\mathbf{x}) = 0 \tag{2.30}$$

i.e. for

$$\hat{O}\psi(\mathbf{x}) = \langle \hat{O} \rangle \psi(\mathbf{x}). \tag{2.31}$$

Thus, if O can be measured sharply, $\psi(\mathbf{x})$ must be an eigenfunction of \hat{O} and the eigenvalue equals the expectation value. No deviations from this eigenvalue occur in the state $\psi(\mathbf{x})$.

Consider two quantities that can be simultaneously measured sharply in all states $\psi_n(\mathbf{x})$, i.e.

$$\begin{aligned}
\hat{O}\psi_n(\mathbf{x}) &= o_n\psi_n(\mathbf{x}) \\
\hat{P}\psi_n(\mathbf{x}) &= p_n\psi_n(\mathbf{x}).
\end{aligned} \tag{2.32}$$

Then holds

$$\hat{O}\hat{P}\psi_n(\mathbf{x}) = \hat{P}\hat{O}\psi_n(\mathbf{x}) \tag{2.33}$$

for all n , yielding

$$[\hat{O}, \hat{P}] = 0 \tag{2.34}$$

Operators that can simultaneously be measured sharply must commute.

2.2 Dirac notation

We noticed that we frequently need to evaluate integrals of the type

$$\int d^3\mathbf{x} \psi(\mathbf{x})^* \varphi(\mathbf{x}). \tag{2.35}$$

To facilitate the notation we write

$$\langle \psi | \varphi \rangle \equiv \int d^3\mathbf{x} \psi(\mathbf{x})^* \varphi(\mathbf{x}). \tag{2.36}$$

This achieves more than just saving to write the integral sign. In fact it turns out that we can consider the abstract functions (as opposed to the values of the function for given \mathbf{x})

$$|\varphi\rangle \text{ and } \langle\psi|. \quad (2.37)$$

Since $\langle\psi|\varphi\rangle$ form a bracket one often calls $\langle\psi|$ a bra vector and $|\varphi\rangle$ a ket vector. The name vector is perfectly adequate as $\langle\psi|\varphi\rangle$ obeys all the properties of a scalar product.

Let us remind of the properties of a scalar product: Take two vectors \mathbf{a} and \mathbf{b} , the scalar product

$$\mathbf{a}^* \cdot \mathbf{b} = \sum_i a_i^* b_i \quad (2.38)$$

obeys

$$\begin{aligned} \mathbf{a}^* \cdot (\lambda\mathbf{b}) &= \lambda (\mathbf{a}^* \cdot \mathbf{b}) \\ \mathbf{a}^* \cdot \mathbf{b} &= (\mathbf{b}^* \cdot \mathbf{a})^* \\ \mathbf{a}^* \cdot (\mathbf{b} + \mathbf{c}) &= \mathbf{a}^* \cdot \mathbf{b} + \mathbf{a}^* \cdot \mathbf{c} \\ \mathbf{a}^* \cdot \mathbf{a} &\geq 0. \end{aligned} \quad (2.39)$$

One can generalize the scalar product to more general Hilbert spaces (essentially all Banach spaces, i.e. spaces with a norm, in which a scalar product can be defined sensibly) and it follows immediately from our above definition of $\langle\psi|\varphi\rangle$ that:

$$\begin{aligned} \langle\psi|\lambda\varphi\rangle &= \lambda \langle\psi|\varphi\rangle \\ \langle\varphi|\psi\rangle^* &= \langle\psi|\varphi\rangle \\ \langle\psi|\varphi + \varphi'\rangle &= \langle\psi|\varphi\rangle + \langle\psi|\varphi'\rangle. \\ \langle\psi|\psi\rangle &\geq 0. \end{aligned} \quad (2.40)$$

In this sense is $\langle\psi|\varphi\rangle$ also considered the *projection* of $|\varphi\rangle$ on $|\psi\rangle$. If they are *orthogonal* it follows $\langle\psi|\varphi\rangle = 0$.

One can then analyze the action of an operator on a bra or ket. Let

$$|\varphi\rangle = \widehat{O} |\psi'\rangle \quad (2.41)$$

then

$$\langle\psi|\varphi\rangle = \langle\psi|\widehat{O}|\psi'\rangle = \langle\psi\widehat{O}^\dagger|\psi'\rangle \quad (2.42)$$

where the last equation means to apply the operator \widehat{O}^\dagger on the bra $\langle\psi|$ and then to take the scalar product of the result with the ket $|\psi'\rangle$. It defines the adjointed operator \widehat{O}^\dagger to \widehat{O} . It holds that the adjointed of the adjointed is the operator himself:

$$\begin{aligned} \langle\psi|\widehat{O}|\psi'\rangle &= \langle\psi\widehat{O}^\dagger|\psi'\rangle = \langle\psi'|\widehat{O}\psi\rangle^* \\ &= \langle\psi'(\widehat{O}^\dagger)^\dagger|\psi\rangle^* = \langle\psi|(\widehat{O})^\dagger|\psi'\rangle \end{aligned} \quad (2.43)$$

or simply:

$$\widehat{O} = (\widehat{O}^\dagger)^\dagger. \quad (2.44)$$

Obviously, self-adjointed operators, with $\widehat{O} = \widehat{O}^\dagger$ are our Hermitian operators that represent physical observables.

Looking at two operators it holds

$$\begin{aligned} \langle \psi | \widehat{O}\widehat{P} | \psi' \rangle &= \langle \psi \widehat{O}^\dagger | \widehat{P} | \psi' \rangle = \langle \psi \widehat{P}^\dagger \widehat{O}^\dagger | \psi' \rangle \\ &= \langle \psi | (\widehat{O}\widehat{P})^\dagger | \psi' \rangle \end{aligned} \quad (2.45)$$

which implies in an operator language

$$(\widehat{O}\widehat{P})^\dagger = \widehat{P}^\dagger \widehat{O}^\dagger. \quad (2.46)$$

Thus, the product of two Hermitian operators is Hermitian itself only if the two operators commute.

Expanding a function in terms of a complete set corresponds to

$$|\psi\rangle = \sum_n a_n |\varphi_n\rangle = \sum_n a_n |n\rangle \quad (2.47)$$

where the last equal sign introduces a common notation. If the $|\varphi_n\rangle$ or simply $|n\rangle$ are eigenfunctions of the operator it holds

$$\widehat{O} |n\rangle = o_n |n\rangle. \quad (2.48)$$

Normalization corresponds to

$$\langle n|m\rangle = \delta_{nm} \quad (2.49)$$

and the action of \widehat{O} on $|\psi\rangle$ corresponds to

$$\widehat{O} |\psi\rangle = \sum_n a_n o_n |n\rangle \quad (2.50)$$

such that the expectation value is

$$\langle \psi | \widehat{O} | \psi \rangle = \sum_{n,m} a_n^* a_m o_m \langle n|m\rangle = \sum_n |a_n|^2 o_n \quad (2.51)$$

Clearly the projection a_n is

$$\langle n|\psi\rangle = \sum_m a_m \langle n|m\rangle = a_n \quad (2.52)$$

and the condition

$$\sum_n |a_n|^2 = 1 \quad (2.53)$$

yields

$$1 = \sum_n \langle n|\psi\rangle^* \langle n|\psi\rangle = \sum_n \langle\psi|n\rangle \langle n|\psi\rangle = \langle\psi|\psi\rangle \quad (2.54)$$

which leads to the operator identity

$$\hat{1} = \sum_n |n\rangle \langle n|. \quad (2.55)$$

In this sense one can also define the operator

$$\hat{R}_{lm} = |l\rangle \langle m| \quad (2.56)$$

which has the property

$$\hat{R}_{lm} |\psi\rangle = \sum_n a_n \hat{O}_{lm} |n\rangle = \sum_n a_n |l\rangle \langle m|n\rangle = a_m |l\rangle. \quad (2.57)$$

A particular appeal of this approach is that it leads to a formulation of quantum mechanics using a matrix formulation. Take the complete set $\{|n\rangle\}$. Then the Schrödinger equation

$$\hat{H} |\psi\rangle = E |\psi\rangle \quad (2.58)$$

can be written as

$$\sum_n a_n \hat{H} |n\rangle = E \sum_n a_n |n\rangle \quad (2.59)$$

We multiply this from the left with the bra $\langle m|$ and it follows

$$\sum_n \langle m| \hat{H} |n\rangle a_n = E a_m \quad (2.60)$$

If we call

$$\mathcal{H}_{mn} = \langle m| \hat{H} |n\rangle \quad (2.61)$$

the m, n matrix element of the matrix \mathcal{H} and a_n the n -th component of the vector \mathbf{a} then the stationary Schrödinger equation reads

$$\mathcal{H} \cdot \mathbf{a} = E \mathbf{a} \quad (2.62)$$

with ordinary matrix multiplication. Similarly we can write for two operators

$$\hat{O} \hat{P} |\psi\rangle \quad (2.63)$$

that

$$\begin{aligned} \langle m| \hat{O} \hat{P} |\psi\rangle &= \sum_{n,l} \langle m| \hat{O} |n\rangle \langle n| \hat{P} |l\rangle a_l \\ &= \sum_{n,l} \mathcal{O}_{mn} \mathcal{P}_{nl} a_l = (\mathcal{O} \mathcal{P} \cdot \mathbf{a})_m \end{aligned} \quad (2.64)$$

2.3 The momentum representation

We discussed that one can expand the wave function in a complete set of functions

$$\psi(x) = \sum_n a_n \varphi_n(x) \quad (2.65)$$

where $\varphi_n(x)$ are the eigenfunctions of an operator \widehat{O} , i.e. $\widehat{O}\varphi_n(x) = o_n\varphi_n(x)$. Then $|a_n|^2$ is the probability for O to take the value o_n . It is then natural to ask what happens if the operator \widehat{O} is the momentum operator \widehat{p} or the position operator \widehat{x} . Since they have a continuous spectrum we write instead

$$\psi(x) = \int dp a_p \varphi_p(x) \quad (2.66)$$

where the eigenfunctions of the momentum operator are

$$\varphi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \quad (2.67)$$

Similarly holds for the position operator

$$\psi(x) = \int dx' a_{x'} \eta_{x'}(x) \quad (2.68)$$

with

$$\widehat{x}\eta_{x'}(x) = x'\eta_{x'}(x). \quad (2.69)$$

The eigenfunctions $\eta_{x'}(x)$ can be most easily identified if one realizes that

$$\psi(x) = a_x \quad (2.70)$$

since both $|\psi(x)|^2$ and $|a_x|^2$ are the probability density to find the particle at position x . Thus, it holds

$$\eta_{x'}(x) = \delta(x - x'). \quad (2.71)$$

Similarly we may write in bra-ket notation

$$|\psi\rangle = \int dp |p\rangle \langle p|\psi\rangle = \int dx |x\rangle \langle x|\psi\rangle \quad (2.72)$$

and we can identify

$$\psi(x) = \langle x|\psi\rangle. \quad (2.73)$$

This suggests to introduce the wave function in momentum representation

$$\psi(p) = \langle p|\psi\rangle. \quad (2.74)$$

What is the representation of \widehat{p} and \widehat{x} in this new representation.

In position representation holds obviously

$$\langle x | \hat{x} | \psi \rangle = x \psi(x) \quad (2.75)$$

and

$$\begin{aligned} \langle x | \hat{p} | \psi \rangle &= \int dp' \langle x | p' \rangle \langle p' | \hat{p} | \psi \rangle \\ &= \int dp' \langle x | p' \rangle p' \langle p' | \psi \rangle. \end{aligned} \quad (2.76)$$

Using $\langle x | p' \rangle = \varphi_{p'}(x)$ it holds

$$p' \langle x | p' \rangle = \frac{\hbar}{i} \frac{\partial}{\partial x} \varphi_{p'}(x). \quad (2.77)$$

Thus it follows the familiar result:

$$\langle x | \hat{p} | \psi \rangle = \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x). \quad (2.78)$$

We can proceed along the same lines and analyze

$$\langle p | \hat{x} | \psi \rangle = \int dx' \langle p | x' \rangle x' \langle x' | \psi \rangle. \quad (2.79)$$

Since $\langle p | x' \rangle = \langle x | p' \rangle^*$ follows

$$\langle p | \hat{x} | \psi \rangle = -\frac{\hbar}{i} \frac{\partial}{\partial p} \psi(p). \quad (2.80)$$

Similarly follows

$$\langle p | \hat{p} | \psi \rangle = p \psi(p). \quad (2.81)$$

If we start from a Hamiltonian

$$H = \frac{\hat{p}^2}{2m} + V(\hat{x}) \quad (2.82)$$

it follows in momentum representation

$$H = \frac{p^2}{2m} + V(i\hbar\nabla_p). \quad (2.83)$$

2.3.1 Particle in a homogeneous field

The problem of a particle in a homogeneous field is characterized by the potential

$$V(x) = -Fx \quad (2.84)$$

leading in position representation to

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} - Fx\psi(x) = E\psi(x) \quad (2.85)$$

which is, as usual, a second order differential equation.

In momentum space the Schrödinger equation is however only a first order differential equation

$$\frac{p^2}{2m}\psi(p) - i\hbar F \frac{d\psi(p)}{dp} = E\psi(p). \quad (2.86)$$

This is equivalent to

$$-i \frac{d\psi}{\psi} = \frac{1}{\hbar F} \left(E - \frac{p^2}{2m} \right) dp. \quad (2.87)$$

Integrating this equation on both sides yields

$$-i \log \frac{\psi(q)}{\psi_0} = \frac{1}{\hbar F} \left(Ep - \frac{p^3}{6m} \right) \quad (2.88)$$

with integration constant ψ_0 . This gives

$$\psi(q) \propto \exp \left(i \frac{E}{\hbar F} p - i \frac{p^3}{6m\hbar F} \right). \quad (2.89)$$

Returning to position space yields

$$\begin{aligned} \psi(x) &= \int \frac{dp}{\sqrt{2\pi\hbar}} e^{i\frac{px}{\hbar}} \psi(q) \\ &\propto \int dp e^{i \left[\frac{p}{\hbar} \left(x + \frac{E}{F} \right) - \frac{p^3}{6m\hbar F} \right]}. \end{aligned} \quad (2.90)$$

Energy enters only via the position

$$x_0 = -\frac{E}{F} \quad (2.91)$$

which corresponds to $E = V(x_0)$, the classical turning point for a particle moving towards negative x .

Introducing

$$\begin{aligned} p &= (2m\hbar F)^{1/3} u \\ \xi &= \left(x + \frac{E}{F} \right) \left(\frac{2mF}{\hbar^2} \right)^{1/3} \end{aligned} \quad (2.92)$$

gives

$$\psi(\xi) = A \int du \cos \left(\frac{u^3}{3} - \xi u \right). \quad (2.93)$$

Given the following representation of the Airy function

$$Ai(\xi) = \int \frac{du}{\pi} \cos \left(\frac{u^3}{3} + \xi u \right) \quad (2.94)$$

it follows

$$\psi(\xi) \propto Ai(-\xi). \quad (2.95)$$

The behavior away from x_0 is characterized by the asymptotic behavior of the Airy function:

$$Ai(\xi) = \begin{cases} \frac{e^{-\frac{2}{3}\xi^{3/2}}}{\sqrt{4\pi}\xi^{1/4}} & \xi > 0 \\ \frac{\sin(\frac{2}{3}|\xi|^{3/2} + \frac{\pi}{4})}{\sqrt{\pi}|\xi|^{1/4}} & \xi < 0 \end{cases}. \quad (2.96)$$

For $x > x_0$ the wave function oscillates while it decays for $x < x_0$.

2.4 The Uncertainty principle

We have established above that two physical quantities can be sharply measured simultaneously if they are represented by operators \hat{O} and \hat{P} that commute, i.e. for

$$[\hat{O}, \hat{P}] = 0. \quad (2.97)$$

Next we will discuss what happens if we consider two operators that do not commute

$$[\hat{O}, \hat{P}] = i\hat{R} \quad (2.98)$$

It obviously holds that \hat{R} is Hermitian if \hat{O} and \hat{P} are:

$$\hat{R} = \frac{\hat{O}\hat{P} - \hat{P}\hat{O}}{i} \quad (2.99)$$

and

$$\hat{R}^\dagger = -\frac{\hat{P}\hat{O} - \hat{O}\hat{P}}{i} = \hat{R} \quad (2.100)$$

We now look at

$$\Delta\hat{O} = \hat{O} - \langle \hat{O} \rangle \quad \text{and} \quad \Delta\hat{P} = \hat{P} - \langle \hat{P} \rangle \quad (2.101)$$

and it follows

$$[\Delta\hat{O}, \Delta\hat{P}] = i\hat{R} \quad (2.102)$$

We first prove the *Schwarz inequality*

$$\langle \alpha | \alpha \rangle \langle \beta | \beta \rangle \geq |\langle \alpha | \beta \rangle|^2 \quad (2.103)$$

for two functions of a set that obey $\langle \alpha | \alpha \rangle \geq 0$ (i.e. not necessarily normalized to unity). To show that this is correct we start from

$$\langle (\alpha | + \lambda^* \langle \beta |) (|\alpha \rangle + \lambda |\beta \rangle) \rangle \geq 0 \quad (2.104)$$

where λ can be any complex number. The inequality must in particular hold when

$$\lambda = -\frac{\langle \beta | \alpha \rangle}{\langle \beta | \beta \rangle} \quad (2.105)$$

This yields

$$\langle \alpha | \alpha \rangle - \frac{|\langle \alpha | \beta \rangle|^2}{\langle \beta | \beta \rangle} - \frac{|\langle \alpha | \beta \rangle|^2}{\langle \beta | \beta \rangle} + \frac{|\langle \alpha | \beta \rangle|^2}{\langle \beta | \beta \rangle} \geq 0 \quad (2.106)$$

which leads to the *Schwarz inequality*. If we now use

$$|\alpha\rangle = \Delta\hat{O}|\psi\rangle \quad (2.107)$$

$$|\beta\rangle = \Delta\hat{P}|\psi\rangle \quad (2.108)$$

Then

$$\langle (\Delta\hat{O})^2 \rangle = \langle \psi | \Delta\hat{O}\Delta\hat{O} | \psi \rangle = \langle \alpha | \alpha \rangle \quad (2.109)$$

and similarly

$$\langle (\Delta\hat{P})^2 \rangle = \langle \beta | \beta \rangle \quad (2.110)$$

and it follows

$$\langle (\Delta\hat{O})^2 \rangle \langle (\Delta\hat{P})^2 \rangle \geq |\langle \psi | \Delta\hat{O}\Delta\hat{P} | \psi \rangle|^2 \quad (2.111)$$

For the right hand side we use $i\hat{R}$

$$\begin{aligned} \Delta\hat{O}\Delta\hat{P} &= \frac{1}{2} [\Delta\hat{O}, \Delta\hat{P}] + \frac{1}{2} (\Delta\hat{O}\Delta\hat{P} + \Delta\hat{P}\Delta\hat{O}) \\ &= \frac{i}{2}\hat{R} + \frac{1}{2} (\Delta\hat{O}\Delta\hat{P} + \Delta\hat{P}\Delta\hat{O}) \end{aligned} \quad (2.112)$$

Thus

$$\langle \psi | \Delta\hat{O}\Delta\hat{P} | \psi \rangle = \frac{i}{2} \langle \hat{R} \rangle + \frac{1}{2} \langle \Delta\hat{O}\Delta\hat{P} + \Delta\hat{P}\Delta\hat{O} \rangle \quad (2.113)$$

with real expectation values $\langle \hat{R} \rangle$ and $\langle \Delta\hat{O}\Delta\hat{P} + \Delta\hat{P}\Delta\hat{O} \rangle$. Thus

$$|\langle \psi | \Delta\hat{O}\Delta\hat{P} | \psi \rangle|^2 \geq \frac{1}{4} \langle \hat{R} \rangle^2 \quad (2.114)$$

and we obtain

$$\langle (\Delta\hat{O})^2 \rangle \langle (\Delta\hat{P})^2 \rangle \geq \frac{1}{4} |\langle [\hat{O}, \hat{P}] \rangle|^2 \quad (2.115)$$

Thus, if two operators do not commute, they cannot be measured sharply at the same time. Another consequence of Eq.2.115 refers to quantities O that can be sharply measured, i.e. for which holds that $\langle (\Delta\hat{O})^2 \rangle = 0$. The uncertainty relation obviously states that for all physical quantities \hat{P} that do not commute with \hat{O} follows $\langle (\Delta\hat{P})^2 \rangle \rightarrow \infty$. Such observables are fully undetermined. If we take for example $\hat{O} = \hat{x}_\alpha$ and $\hat{P} = \hat{p}_\beta$ it follows with

$$[\hat{p}_\alpha, \hat{x}_\beta] = \frac{\hbar}{i} \delta_{\alpha\beta} \quad (2.116)$$

that

$$\langle (\Delta \hat{p}_\alpha)^2 \rangle \langle (\Delta \hat{x}_\beta)^2 \rangle \geq \frac{\hbar^2}{4} \delta_{\alpha\beta} \quad (2.117)$$

In particular holds for a plane wave, with $\langle (\Delta \hat{p}_\alpha)^2 \rangle = 0$ that the position of the particle is completely undetermined.

Chapter 3

The harmonic oscillator

We consider a particle in an harmonic oscillator potential

$$V(x) = \frac{k}{2}x^2 \quad (3.1)$$

where k is the force constant. We know that classical particles oscillate in this potential with frequency

$$\omega = \sqrt{\frac{k}{m}}. \quad (3.2)$$

The Hamilton operator of the problem is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{k}{2}x^2. \quad (3.3)$$

The stationary Schrödinger equation

$$\hat{H}\psi = E\psi \quad (3.4)$$

is then given as

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{k}{2}x^2\psi(x) = E\psi(x), \quad (3.5)$$

which we rewrite as

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{k}{2}x^2 \right) \psi(x) = 0. \quad (3.6)$$

A dimensional analysis yields: $[k] = \frac{\text{energy}}{\text{length}^2}$, $[\hbar\omega] = \text{energy}$, implying that

$$\frac{m\omega}{\hbar} = \frac{k}{\hbar\omega} \quad (3.7)$$

carries unit of inverse length square. Thus,

$$\xi = \sqrt{\frac{m\omega}{\hbar}}x \quad (3.8)$$

is a dimensionless quantity. In what follows perform a substitution of variables to the dimensionless length ξ . We furthermore introduce the dimensionless scale

$$\varepsilon = \frac{2E}{\hbar\omega} \quad (3.9)$$

and obtain the Schrödinger equation in dimensionless units:

$$\frac{d^2\psi}{d\xi^2} + (\varepsilon - \xi^2)\psi = 0. \quad (3.10)$$

We first analyze the asymptotic solution for large ξ , where $\xi^2 \gg \max\{1, \varepsilon\}$. Then we only need to solve

$$\frac{d^2\psi}{d\xi^2} = \xi^2\psi. \quad (3.11)$$

In order to determine the solution of this differential equation we multiply the equation by $2\frac{d\psi}{d\xi}$, yielding

$$\frac{d}{d\xi} \left(\frac{d\psi}{d\xi} \right)^2 = \xi^2 \frac{d}{d\xi} \psi^2. \quad (3.12)$$

A similar approach worked fine in case of Newton's equation. Now however the problem is explicitly ξ -dependent and the solution is more subtle. For our purposes it is however sufficient to approximately solve the equation for large ξ (elsewhere it isn't valid anyway). We have

$$\frac{d}{d\xi} \left(\left(\frac{d\psi}{d\xi} \right)^2 - \xi^2 \psi^2 \right) = -2\xi \psi^2 \quad (3.13)$$

If the r.h.s. of the equation is negligible, we only have to solve

$$\frac{d}{d\xi} \left(\left(\frac{d\psi}{d\xi} \right)^2 - \xi^2 \psi^2 \right) = 0 \quad (3.14)$$

which yields

$$\frac{d\psi}{d\xi} = \pm \sqrt{C + \xi^2 \psi^2}. \quad (3.15)$$

Since both ψ and $\frac{d\psi}{d\xi}$ vanish as $\xi \rightarrow \infty$ it must hold that $C = 0$. Thus

$$\frac{d\psi}{d\xi} = \pm \xi \psi \quad (3.16)$$

Thus

$$\frac{d\psi}{\psi} = \pm \xi d\xi \quad (3.17)$$

Integrating this differential equation finally gives

$$\psi = c \exp\left(-\frac{1}{2}\xi^2\right), \quad (3.18)$$

where we ignored the solution with + as it yields a wave function that diverges as $\xi \rightarrow \infty$. It is easy to check that $\xi\psi^2$ is indeed small compared to the other terms, justifying our earlier assumption. Alternatively we can just insert this solution into Eq.3.11. It holds

$$\frac{d^2\psi}{d\xi^2} = (\xi^2 - 1) \psi \simeq \xi^2 \psi, \quad (3.19)$$

as required.

The asymptotic analysis suggest to make the following ansatz for the wave function for arbitrary ξ :

$$\psi(\xi) = h(\xi) \exp\left(-\frac{1}{2}\xi^2\right). \quad (3.20)$$

Substitution of this ansatz into Eq.3.10 gives:

$$h''(\xi) - 2\xi h'(\xi) + (\varepsilon - 1)h = 0. \quad (3.21)$$

The boundary condition for $h(\xi)$ are that it doesn't grow faster than $\exp(\frac{1}{2}\xi^2)$ as $\xi \rightarrow \pm\infty$. Otherwise the $\exp(-\frac{1}{2}\xi^2)$ may not be able to compensate the growths at large ξ . Furthermore, $h(\xi)$ is not allowed to diverge anywhere for finite ξ .

Since $h(\xi)$ does not diverge for finite ξ it can be written as a power series with non-negative powers:

$$h(\xi) = \sum_{n=0}^{\infty} a_n \xi^n. \quad (3.22)$$

Inserting this series into the above differential equation gives

$$\begin{aligned} h''(\xi) &= \sum_{n=2}^{\infty} a_n n(n-1) \xi^{n-2} = \sum_{m=0}^{\infty} a_{m+2} (m+2)(m+1) \xi^m \\ -2\xi h'(\xi) &= -2 \sum_{n=1}^{\infty} a_n n \xi^n = -2 \sum_{m=0}^{\infty} a_m m \xi^m \\ (\varepsilon - 1)h(\xi) &= (\varepsilon - 1) \sum_{m=0}^{\infty} a_m \xi^m. \end{aligned} \quad (3.23)$$

In order to fulfill the differential equation the coefficients for each power have to vanish independently, i.e.

$$\sum_{m=0}^{\infty} [a_{m+2} (m+2)(m+1) - 2a_m m + (\varepsilon - 1)a_m] \xi^m = 0 \quad (3.24)$$

which yields

$$a_{m+2} (m+2)(m+1) + (\varepsilon - 2m - 1)a_m = 0. \quad (3.25)$$

Thus, we obtain the recursion relation:

$$a_{m+2} = \frac{(2m+1-\varepsilon)}{(m+2)(m+1)} a_m. \quad (3.26)$$

Given a_0 and a_1 all a_m are determined by Eq.3.26. For large m it follows

$$a_{m+2} \simeq \frac{2}{m} a_m \quad (3.27)$$

To get a better interpretation of this result we search for a known function with similar recursion relation of the power series expansion. We expand

$$e^{\xi^2} = \sum_m \frac{\xi^{2m}}{m!}. \quad (3.28)$$

The coefficient b_m of ξ^m is

$$b_m = \frac{1}{(m/2)!}. \quad (3.29)$$

Thus it follows

$$b_{m+2} = \frac{1}{(\frac{m}{2}+1)!} = \frac{1}{\frac{m}{2}+1} \frac{1}{\frac{m}{2}!} = \frac{2}{m+2} b_m. \quad (3.30)$$

For large m this implies

$$b_{m+2} \simeq \frac{2}{m} b_m. \quad (3.31)$$

We conclude that our polynomial ansatz behaves for large ξ (where large m are relevant) as e^{ξ^2} which diverges faster than $\exp(\frac{1}{2}\xi^2)$. Thus, we have to reject the solution that allows $a_m \neq 0$ for arbitrary large m .

The only way out is to restrict the power series to a finite number of terms. This can be achieved if ε equals $2n+1$ with some integer n . Thus we find

$$\varepsilon_n = \frac{2E_n}{\hbar\omega} = 2n+1 \quad (3.32)$$

or

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right). \quad (3.33)$$

and $n = 0, 1, \dots$. The requirement to have a wave function that vanishes at infinity is again the origin for energy quantization. We observe that, in distinction to the potential well, the difference between two consecutive eigenvalues is constant $E_{n+1} - E_n = \hbar\omega$. This is reminiscent of the behavior one encounters in case of photons. One way to interpret this result is to say that there are n non-interacting elementary quanta in the system each contributing an energy $\hbar\omega$ to the total energy. In this sense is n the number of such quanta.

For a given n the recursion relation of the coefficients a_m is:

$$a_{m+2} = \frac{2(m-n)}{(m+2)(m+1)} a_m \quad (3.34)$$

which yields $a_{m+2} = 0$ for $m > n$. However the condition $\varepsilon_n = 2n + 1$ can only stop the recursion for either the coefficients of even or of odd powers in ξ . Thus, to avoid that the power series grows as e^{ξ^2} we require $a_0 = 0$ if n odd and $a_1 = 0$ if n even. Thus we find

$$\psi_n(\xi) = (-1)^n \psi_n(-\xi). \quad (3.35)$$

The wave functions are either even or odd. In case of the infinitely deep potential well we already realized that the solution of the Schrödinger equation for a symmetric potential $V(x) = V(-x)$ led to solutions that were even or that were odd under reflection. The same holds for the harmonic oscillator.

The lowest energy is not zero but $\frac{\hbar\omega}{2}$, called zero point energy. It is a natural consequence of the uncertainty principle. To see this we estimate

$$E \simeq \frac{p_{\text{typ}}^2}{2m} + \frac{k}{2} x_{\text{typ}}^2 \quad (3.36)$$

with typical momentum and position values, consistent with the uncertainty principle. Thus we obtain

$$\begin{aligned} p_{\text{typ}}^2 &\simeq \langle (\Delta\hat{p})^2 \rangle \simeq \frac{\hbar^2}{4 \langle (\Delta\hat{x})^2 \rangle} \\ x_{\text{typ}}^2 &\simeq \langle (\Delta\hat{x})^2 \rangle, \end{aligned} \quad (3.37)$$

which yields

$$E \simeq \frac{\hbar^2}{4 \langle (\Delta\hat{x})^2 \rangle} \frac{1}{2m} + \frac{k}{2} \langle (\Delta\hat{x})^2 \rangle. \quad (3.38)$$

Minimizing this w.r.t. $\langle (\Delta\hat{x})^2 \rangle$ gives

$$\langle (\Delta\hat{x})^2 \rangle = \frac{\hbar}{2\sqrt{km}} \quad (3.39)$$

and then

$$E \simeq \frac{1}{4}\hbar\omega_0 + \frac{1}{4}\hbar\omega_0 = \frac{1}{2}\hbar\omega_0. \quad (3.40)$$

This is even the exact result. Important is that it gives us the correct order of magnitude.

Lets return to our determination of the eigenfunctions. The solution $h_n(\xi)$ is therefore an easy to determine polynomial. For the ground state holds $a_{m=0} = \text{const}$ and $a_{m>1} = 0$.

$$h(\xi) = \text{const}. \quad (3.41)$$

where the constant is determined by normalization. Thus we obtain for the ground state wave function

$$\psi(\xi) \propto \exp\left(-\frac{1}{2}\xi^2\right). \quad (3.42)$$

Returning to the original length scale x and normalizing the wave function gives:

$$\psi(x) = \frac{1}{\sqrt{2}} \left(\frac{m\omega}{\hbar\pi} \right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar}x^2\right). \quad (3.43)$$

In general we can write for the wave function that

$$\psi_n(x) = C_n H_n \left(\sqrt{\frac{m\omega}{\hbar}} x \right) \exp\left(-\frac{m\omega}{2\hbar}x^2\right) \quad (3.44)$$

where the $H_n(\xi)$ are the Hermite polynomials. Using our recursion relation yields

$$\begin{aligned} H_0(\xi) &= 1 \\ H_1(\xi) &= 2\xi \\ H_2(\xi) &= -2 + 4\xi^2 \\ H_3(\xi) &= -12\xi + 8\xi^3 \\ H_4(\xi) &= 12 + 48\xi^2 + 16\xi^4 \\ H_5(\xi) &= 120\xi - 160\xi^3 + 32\xi^5 \end{aligned} \quad (3.45)$$

The so defines Hermite polynomial obey relations such as:

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2} = e^{\frac{\xi^2}{2}} \left(\xi - \frac{d}{d\xi} \right)^n e^{-\frac{\xi^2}{2}} \quad (3.46)$$

and have the property

$$\int d\xi H_n(\xi) H_m(\xi) e^{-\xi^2} = \sqrt{\pi} 2^n n! \delta_{nm} \quad (3.47)$$

This allows us to determine the normalization coefficient

$$C_n = \frac{2^{-n/2}}{\sqrt{n!}} \left(\frac{m\omega}{\hbar\pi} \right)^{1/4} \quad (3.48)$$

of the wave function.

We could now proceed and evaluate matrix elements such as $\langle n | \hat{x} | m \rangle$ or $\langle n | \hat{p} | m \rangle$ using properties of the Hermite polynomials. It turns out however that there is an easier and more elegant way to look at the problem. We already realized that $\xi = \sqrt{\frac{m\omega}{\hbar}}x$ is an appropriate dimensionless length scale. equally, $\sqrt{\frac{1}{\hbar m\omega}}p$ is a dimensionless momentum variable. We therefore introduce a dimensionless combination

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + \frac{i}{m\omega} \hat{p} \right) = \frac{1}{\sqrt{2}} \left(\xi + \frac{d}{d\xi} \right) \quad (3.49)$$

which is not a Hermitian operator. Its adjoint operator is

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i}{m\omega} \hat{p} \right) = \frac{1}{\sqrt{2}} \left(\xi - \frac{d}{d\xi} \right) \quad (3.50)$$

The virtue of these operators is that they obey very simple commutation relations:

$$\begin{aligned} [\hat{a}, \hat{a}^\dagger] &= \frac{m\omega}{2\hbar} \left[\hat{x} + \frac{i}{m\omega} \hat{p}, \hat{x} - \frac{i}{m\omega} \hat{p} \right] \\ &= -\frac{i}{2\hbar} [\hat{x}, \hat{p}] + \frac{i}{2\hbar} [\hat{p}, \hat{x}] = 1. \end{aligned} \quad (3.51)$$

We also define the operator

$$\hat{N} = \hat{a}^\dagger \hat{a} \quad (3.52)$$

which is Hermitian and thus represents a physical observable ($\hat{N}^\dagger = (\hat{a}^\dagger \hat{a})^\dagger = \hat{a}^\dagger \hat{a} = \hat{N}$). It holds

$$\begin{aligned} \hat{N} &= \frac{m\omega}{2\hbar} \left(\hat{x} - \frac{i}{m\omega} \hat{p} \right) \left(\hat{x} + \frac{i}{m\omega} \hat{p} \right) \\ &= \frac{m\omega}{2\hbar} \hat{x}^2 + \frac{1}{2m\hbar\omega} \hat{p}^2 - \frac{i}{2\hbar} [\hat{p}, \hat{x}] \\ &= \frac{1}{\hbar\omega} \left(\frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2} \hat{x}^2 \right) - \frac{1}{2}. \end{aligned} \quad (3.53)$$

We therefore obtain

$$\hat{H} = \hbar\omega \left(\hat{N} + \frac{1}{2} \right). \quad (3.54)$$

Since the eigenvalues of \hat{H} are given as $E_n = \hbar\omega (n + \frac{1}{2})$ we conclude that the eigenvalues of the operator \hat{N} are the integers n that determine the eigenstates of the harmonic oscillator.

$$\hat{N} |n\rangle = n |n\rangle. \quad (3.55)$$

We can also give a specific interpretation to the operators \hat{a} and \hat{a}^\dagger . We first analyze

$$\begin{aligned} [\hat{N}, \hat{a}] &= [\hat{a}^\dagger \hat{a}, \hat{a}] = \hat{a}^\dagger \hat{a} \hat{a} - \hat{a} \hat{a}^\dagger \hat{a} \\ &= \hat{a} \hat{a}^\dagger \hat{a} - \hat{a} - \hat{a} \hat{a}^\dagger \hat{a} = -\hat{a}. \end{aligned} \quad (3.56)$$

Likewise we find the adjoint equation

$$[\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger \quad (3.57)$$

As a result, we have

$$\begin{aligned} \hat{N} \hat{a}^\dagger |n\rangle &= [\hat{N}, \hat{a}^\dagger] |n\rangle + \hat{a}^\dagger \hat{N} |n\rangle \\ &= (n+1) \hat{a}^\dagger |n\rangle. \end{aligned} \quad (3.58)$$

and

$$\begin{aligned} \hat{N} \hat{a} |n\rangle &= [\hat{N}, \hat{a}] |n\rangle + \hat{a} \hat{N} |n\rangle \\ &= (n-1) \hat{a} |n\rangle. \end{aligned} \quad (3.59)$$

We conclude that $\hat{a}^\dagger |n\rangle$ is an eigenstate to \hat{N} with eigenvalue increased by one and similarly $\hat{a} |n\rangle$ an eigenstate with an eigenvalue decreased by one. Thus

$$\hat{a} |n\rangle = c |n-1\rangle \quad (3.60)$$

where c is a numerical constant. to be determines from the condition that $|n\rangle$ and $|n-1\rangle$ are normalized. It holds

$$\langle n | \hat{a}^\dagger = c^* \langle n-1 | \quad (3.61)$$

and we conclude

$$\langle n | \hat{a}^\dagger \hat{a} |n\rangle = |c|^2 \langle n-1 | n-1\rangle \quad (3.62)$$

which gives $|c|^2 = n$ and we find

$$\hat{a} |n\rangle = \sqrt{n} |n-1\rangle. \quad (3.63)$$

Similarly it follows

$$\hat{a}^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle. \quad (3.64)$$

The operator \hat{a}^\dagger and \hat{a} raise and lower the quantum number (i.e. the number of quanta). For these reasons, these operators are often called creation and annihilation operators. Nowhere in our analysis did we really need to assume that the eigenvalues n of \hat{N} are integers. However, the result $\hat{a} |n\rangle = \sqrt{n} |n-1\rangle$ implies that we can generate lower and lower eigenstates with energies unbounded from below. Since this is not what we expect, the only way out is to request that the n are integers. Then

$$\hat{a} |n=0\rangle = 0 \quad (3.65)$$

and no states with $|n=-1\rangle$ is being generated.

This allows us to determine the wave functions of the harmonic oscillator. The ground state wave function obviously obeys

$$\sqrt{\frac{m\omega}{2\hbar}} \left(x + \frac{\hbar}{m\omega} \frac{d}{dx} \right) \langle x | n=0\rangle = 0 \quad (3.66)$$

which we write as

$$\frac{1}{\sqrt{2}} \left(\xi + \frac{d}{d\xi} \right) \psi_0(\xi) = 0 \quad (3.67)$$

This differential equation has the solution

$$\psi_0(\xi) = A_0 \exp(-\xi^2/2) \quad (3.68)$$

Next we determine the first excited state via

$$|1\rangle = \hat{a}^\dagger |0\rangle \quad (3.69)$$

and higher excited states via

$$\begin{aligned} |2\rangle &= \frac{1}{\sqrt{2}} \hat{a}^\dagger |1\rangle = \frac{1}{\sqrt{2}} (\hat{a}^\dagger)^2 |0\rangle \\ |n\rangle &= \frac{1}{\sqrt{n!}} (\hat{a}^\dagger)^n |0\rangle \end{aligned} \quad (3.70)$$

which we write as

$$\psi_n(\xi) = A_n \left(\xi - \frac{d}{d\xi} \right)^n \exp(-\xi^2/2) \quad (3.71)$$

With our above expression for the Hermite polynomials

$$H_n(\xi) = e^{\xi^2/2} \left(\xi - \frac{d}{d\xi} \right)^n e^{-\xi^2/2} \quad (3.72)$$

follows

$$\psi_n(\xi) = A_n H_n(\xi) e^{-\xi^2/2}. \quad (3.73)$$

The pre-factors A_n are easily by normalizing the wave function and we find the same results for the wave function as before.

Using the above properties of the operators \hat{a} and \hat{a}^\dagger , we easily obtain for an arbitrary matrix element

$$\begin{aligned} \langle m | \hat{a} | n \rangle &= \sqrt{n} \langle m | n-1 \rangle = \sqrt{n} \delta_{m,n-1} \\ \langle m | \hat{a}^\dagger | n \rangle &= \sqrt{n+1} \langle m | n+1 \rangle = \sqrt{n+1} \delta_{m,n+1}. \end{aligned} \quad (3.74)$$

This allows us to determine the matrix elements of the position and momentum operators

$$\begin{aligned} \hat{x} &= \sqrt{\frac{\hbar}{2m\omega}} (\hat{a}^\dagger + \hat{a}) \\ \hat{p} &= i\sqrt{\frac{m\hbar\omega}{2}} (\hat{a}^\dagger - \hat{a}). \end{aligned} \quad (3.75)$$

We obtain

$$\begin{aligned} \langle m | \hat{x} | n \rangle &= \sqrt{\frac{\hbar}{2m\omega}} (\sqrt{n+1} \delta_{m,n+1} + \sqrt{n} \delta_{m,n-1}) \\ \langle m | \hat{p} | n \rangle &= i\sqrt{\frac{m\hbar\omega}{2}} (\sqrt{n+1} \delta_{m,n+1} - \sqrt{n} \delta_{m,n-1}). \end{aligned} \quad (3.76)$$

Of course the same results follow from the explicit analysis of the Hermite polynomials. The beauty of the present approach is that it doesn't actually require knowledge of the wave functions. Also, the formalism outlined here is hugely important in the formulation of many body quantum field theory.

Chapter 4

Additional one-dimensional problems

4.1 One dimensional barriers

We want to study what happens to an incoming particle (originating in a region with vanishing potential) that enters a region with nonzero potential. We consider a stationary process, i.e. we assume that the solution of the Schrödinger equation does not depend on time. Thus, a constant flux of incoming particles is being considered. Later we will discuss scattering theory and discuss to what extent this assumption is realistic and justified.

4.1.1 The step potential

To be specific we consider first the potential

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x \geq 0 \end{cases} \quad (4.1)$$

For $x < 0$ we have to solve the non-interacting Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad (4.2)$$

with solution

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad (4.3)$$

where

$$k = \frac{\sqrt{2mE}}{\hbar} \quad (4.4)$$

depends on the energy of the incoming particle. The currents associated with the two terms are

$$\begin{aligned} j_{inc} &= \frac{\hbar}{2mi} 2ik |A|^2 \\ j_{refl} &= -\frac{\hbar}{2mi} 2ik |B|^2 \end{aligned} \quad (4.5)$$

where we used $j = \frac{\hbar}{2mi} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right)$. This motivates to define the reflection coefficient

$$R = \left| \frac{j_{refl}}{j_{inc}} \right| = \left| \frac{B}{A} \right|^2 \quad (4.6)$$

For $x > 0$ the Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = (E - V_0) \psi(x). \quad (4.7)$$

If $E > V_0$ it follows

$$\psi(x) = C' e^{ik'x} \quad (4.8)$$

with

$$k' = \frac{\sqrt{2m(E - V_0)}}{\hbar}. \quad (4.9)$$

By assumption we neglect a contribution $D e^{-ik'x}$ corresponding to an incoming wave from the $x > 0$ region. If $E < V_0$ the solution is

$$\psi(x) = C e^{-\kappa x} \quad (4.10)$$

where

$$\kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \quad (4.11)$$

and we ignored the exponentially rising solution $\propto e^{\kappa x}$.

For $E < V_0$ the wave function is (except for the x -independent pre-factor C) real and no current is being transmitted ($j_{trans} = j(x > 0) = 0$), while for $E > V_0$ holds

$$j_{trans} = \frac{\hbar}{2mi} 2ik' |C|^2. \quad (4.12)$$

This leads for $E > V_0$ to the transmission coefficient

$$T = 1 - R = \left| \frac{j_{trans}}{j_{inc}} \right| = \frac{k'}{k} \left| \frac{C}{A} \right|^2 \quad (4.13)$$

The relation $T = 1 - R$ follows from the continuity equation $\frac{\partial j}{\partial x} = 0$ of our stationary process that gives

$$j(x \rightarrow -\infty) = j(x \rightarrow \infty). \quad (4.14)$$

Since $j(x \rightarrow -\infty) = j_{inc} + j_{refl}$ and $j(x \rightarrow \infty) = j_{trans}$ follows $j_{inc} + j_{refl} = j_{trans}$ yielding

$$\left| \frac{j_{trans}}{j_{inc}} \right| = 1 - \left| \frac{j_{refl}}{j_{inc}} \right| \quad (4.15)$$

which is equivalent to Eq.4.13.

In order to determine the ratios B/A and C/A we use the boundary conditions at $x = 0$

$$\begin{aligned} \psi(0^+) &= \psi(0^-) \\ \psi'(0^+) &= \psi'(0^-) \end{aligned} \quad (4.16)$$

It follows

$$\begin{aligned} A + B &= C \\ A - B &= \frac{k'}{k}C \end{aligned} \quad (4.17)$$

and we can solve this for

$$\begin{aligned} \frac{C}{A} &= \frac{2}{1 + k'/k} \\ \frac{B}{A} &= \frac{1 - k'/k}{1 + k'/k} \end{aligned} \quad (4.18)$$

and we finally obtain the transmission and reflection coefficients

$$\begin{aligned} T &= \frac{4k'/k}{(1 + k'/k)^2} \\ R &= \left(\frac{1 - k'/k}{1 + k'/k} \right)^2 \end{aligned} \quad (4.19)$$

It furthermore holds

$$\left(\frac{k'}{k} \right)^2 = 1 - \frac{V_0}{E}. \quad (4.20)$$

It follows

$$T = \frac{4\sqrt{1 - \frac{V_0}{E}}}{\left(1 + \sqrt{1 - \frac{V_0}{E}} \right)^2} \quad (4.21)$$

Obviously, $T(E \rightarrow \infty) \rightarrow 1$ and $T(E \rightarrow V_0) \rightarrow 0$. Close to those limits holds

$$\begin{aligned} T(E \simeq V_0) &\simeq 4\sqrt{\frac{E - V_0}{V_0}} \\ T(E \gg V_0) &\simeq 1 - \frac{1}{4} \left(\frac{V_0}{E} \right)^2 \end{aligned} \quad (4.22)$$

In case $E < V_0$ we can again determine the boundary conditions for the wave function and its first derivative to determine C'/A and B/A . It holds

$$\begin{aligned} A + B &= C' \\ A - B &= i \frac{\kappa}{k} C' \end{aligned} \quad (4.23)$$

which yields

$$\frac{C'}{A} = \frac{2}{1 + i\kappa/k} \quad (4.24)$$

$$\frac{B}{A} = \frac{1 - i\kappa/k}{1 + i\kappa/k} \quad (4.25)$$

The expression for B/A is of the form $\frac{z^*}{z} = e^{-i2\phi}$ where $z = re^{i\phi}$. The phase is

$$\phi = \arctan \frac{\kappa}{k} \quad (4.26)$$

which yields $1 + \left(\frac{\kappa}{k}\right)^2 = \frac{1}{\cos^2 \phi}$. Thus we obtain

$$\begin{aligned} \psi(x < 0) &= A \left(e^{ikx} + e^{-i(kx+2\phi)} \right) \\ \psi(x > 0) &= 2A |\cos \phi| e^{-i\phi} e^{-\kappa r} \end{aligned} \quad (4.27)$$

ϕ is called the *phase shift* of the potential

$$\phi = \arctan \frac{\kappa}{k} = \arctan \sqrt{\frac{V_0 - E}{E}} \quad (4.28)$$

It holds

$$\phi \simeq \begin{cases} \frac{\pi}{2} - \sqrt{\frac{E-V_0}{V_0}} & E \ll V_0 \\ \sqrt{\frac{V_0-E}{V_0}} & E \rightarrow V_0 - 0^+ \end{cases} \quad (4.29)$$

4.1.2 Rectangular barrier and tunneling

From our previous analysis we learned that the incoming wave penetrates the potential even if $E < V_0$. Since the potential stays at the value V_0 up to $x \rightarrow \infty$, the particle will eventually decay. It is however interesting to analyze the situation where the potential is finite only in a limited region of space. Thus we analyze the rectangular barrier:

$$V(x) = \begin{cases} 0 & x < -a \\ V_0 & -a \leq x \leq a \\ 0 & a < x \end{cases} \quad (4.30)$$

We have to solve the Schrödinger equation in three different regions: for $x < -a$, for $-a < x < a$ and for $x > a$, separated by two boundaries.

We start with the situation where $E > V_0$. From our previous analysis we know that the solution in the three regions are

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < -a \\ Ce^{ik'x} + De^{-ik'x} & -a \leq x \leq a \\ Fe^{ikx} & a < x \end{cases} \quad (4.31)$$

where,

$$\begin{aligned} k &= \frac{\sqrt{2mE}}{\hbar} \\ k' &= \frac{\sqrt{2m(E - V_0)}}{\hbar}. \end{aligned} \quad (4.32)$$

similar to our previous solution, we do not allow for a reflected, left moving wave in the region $x > a$. We also noticed before that we can only determine the ratios B/A , C/A of the reflected and transmitted amplitudes relative to the incoming amplitude. To simplify the notation we can therefore set $A = 1$, i.e. we measure all amplitudes in units of A . For convenience we introduce the dimensionless strength of the potential

$$\frac{\gamma^2}{4} = \frac{V_0}{\frac{\hbar^2}{2ma^2}} = (ak)^2 - (ak')^2. \quad (4.33)$$

The problem is then characterized by γ and by the dimensionless ratio

$$\varepsilon = \frac{E}{V_0} \quad (4.34)$$

We can furthermore determine the transmission and reflection coefficients

$$\begin{aligned} T &= \left| \frac{j_{trans}}{j_{inc}} \right| = |F|^2 \\ R &= \left| \frac{j_{refl}}{j_{inc}} \right| = |B|^2 \end{aligned} \quad (4.35)$$

We have two boundaries at $x = \pm a$ and two boundary conditions for each boundary. This yields for the first boundary at $x = -a$:

$$\begin{aligned} e^{-ika} + Be^{ika} &= Ce^{-ik'a} + De^{ik'a} \\ k(e^{-ika} - Be^{ika}) &= k'(Ce^{-ik'a} - De^{ik'a}) \end{aligned} \quad (4.36)$$

and for the second boundary at $x = a$

$$\begin{aligned} Ce^{ik'a} + De^{-ik'a} &= Fe^{ika} \\ k'(Ce^{ik'a} - De^{-ik'a}) &= kFe^{ika} \end{aligned} \quad (4.37)$$

The coefficients C and D occur for both boundaries, so it is wise to eliminate them and obtain equations for B and F only, as those are the ones that determine the reflection and transmission coefficients.

The last two equations can be solved for C and D for given F :

$$\begin{aligned} C e^{ik'a} &= \frac{F}{2} \left(1 + \frac{k}{k'}\right) e^{ika} \\ D e^{-ik'a} &= \frac{F}{2} \left(1 - \frac{k}{k'}\right) e^{ika} \end{aligned} \quad (4.38)$$

Substituting this into the first two equations gives

$$\begin{aligned} e^{-ika} + B e^{ika} &= \frac{F e^{ika}}{2} \left(\left(1 + \frac{k}{k'}\right) e^{-2ik'a} + \left(1 - \frac{k}{k'}\right) e^{2ik'a} \right) \\ e^{-ika} - B e^{ika} &= \frac{k'}{k} \frac{F e^{ika}}{2} \left(\left(1 + \frac{k}{k'}\right) e^{-2ik'a} - \left(1 - \frac{k}{k'}\right) e^{2ik'a} \right) \end{aligned}$$

Which can be simplified to

$$\begin{aligned} e^{-ika} + B e^{ika} &= F e^{ika} \cos(2k'a) - i \frac{k}{k'} F e^{ika} \sin(2k'a) \\ e^{-ika} - B e^{ika} &= F e^{ika} \cos(2k'a) - i \frac{k'}{k} F e^{ika} \sin(2k'a) \end{aligned} \quad (4.39)$$

Adding and subtracting these two equations gives

$$\begin{aligned} F &= \frac{2e^{-i2ka}}{\cos(2k'a) - \frac{i}{2} \frac{k^2+k'^2}{k'k} \sin(2k'a)} \\ 2B &= i \frac{k'^2 - k^2}{k'k} F \sin(2k'a) \end{aligned} \quad (4.40)$$

The transmission coefficient is most simply obtained from the second of these, together with the relation

$$T + R = |F|^2 + |B|^2 = 1. \quad (4.41)$$

It follows

$$\frac{1}{T} = \frac{1}{|F|^2} = 1 + \frac{|B|^2}{|F|^2} \quad (4.42)$$

From the second equation above follows

$$\frac{B}{F} = \frac{i}{2} \frac{k'^2 - k^2}{k'k} \sin(2k'a) \quad (4.43)$$

and we find for the transmission coefficient for $E > V_0$

$$\begin{aligned} \frac{1}{T} &= 1 + \frac{1}{4} \left(\frac{k'^2 - k^2}{k'k} \right)^2 \sin^2(2k'a) \\ &= 1 + \frac{1}{4} \frac{V_0^2}{E(E - V_0)} \sin^2(2k'a) \end{aligned} \quad (4.44)$$

In terms of the dimensionless quantities γ and ε follows with $k'a = \frac{\gamma}{2}\sqrt{\varepsilon-1}$

$$T = \frac{1}{1 + \frac{\sin^2(\gamma\sqrt{\varepsilon-1})}{4\varepsilon(\varepsilon-1)}} \quad (4.45)$$

While obviously holds that $T \leq 1$, the transmission is perfect ($T = 1$) for $\sin^2(2k'a)$ i.e. for

$$2k'a = n\pi. \quad (4.46)$$

Setting $k' = 2\pi/\lambda$ with wave length λ this equals to

$$2a = n\frac{\lambda}{2}. \quad (4.47)$$

When the barrier width $2a$ is an integer times half the wave length, the barrier becomes transparent, just like the total transmission of light through thin refracting layers. Written in terms of E and V , the condition for perfect transmission becomes

$$E - V_0 = n^2 \left(\frac{\pi^2 \hbar^2}{8a^2 m} \right) = n^2 E_1 \quad (4.48)$$

where E_1 is the ground state energy of a one dimensional box.

For the case $E < V_0$ the set of equations is identical to the one for $E > V_0$ with the simple modification

$$k' = \frac{i\sqrt{2m(V_0 - E)}}{\hbar} = i\kappa' \quad (4.49)$$

This gives

$$\frac{B}{F} = -\frac{i\kappa'^2 + k^2}{2\kappa'k} \sinh(2\kappa'a) \quad (4.50)$$

and consequently

$$\frac{1}{T} = 1 + \frac{1}{4} \left(\frac{\kappa'^2 + k^2}{\kappa'k} \right)^2 \sinh^2(2\kappa'a) \quad (4.51)$$

Thus

$$T = \frac{1}{1 + \frac{1}{4} \frac{V_0^2}{(V_0 - E)E} \sinh^2(2\kappa'a)} \quad (4.52)$$

The dimensionless variable γ is now given as

$$\frac{\gamma^2}{4} = \frac{V_0}{\frac{\hbar^2}{2ma^2}} = (ak)^2 + (a\kappa')^2 \quad (4.53)$$

and it follows with $\kappa'a = \frac{\gamma}{2}\sqrt{\frac{V_0 - E}{V_0}}$ that in dimensionless units

$$T = \frac{1}{1 + \frac{1}{4} \frac{\sinh^2(\gamma\sqrt{1-\varepsilon})}{(1-\varepsilon)\varepsilon}}. \quad (4.54)$$

For $E = V$ follows with $\sinh(x) \simeq x$ for small x that the transmission coefficient is:

$$T = \frac{1}{1 + \frac{\gamma^2}{4}} < 1. \quad (4.55)$$

The fact that $T > 0$ for $E < V$ is a purely quantum mechanical effect. Particles can pass through barriers that are impenetrable for classical objects, a phenomenon known as *tunneling*. It allows emission of α -particles from a nucleus and field emission from a metal surface in the presence of an electric field.

For large a it follows that γ is large and we can write that

$$\sinh(\gamma\sqrt{1-\varepsilon}) \simeq \frac{1}{2}e^{\gamma\sqrt{1-\varepsilon}} \quad (4.56)$$

and it follows

$$\gamma = 2\sqrt{\frac{V_0}{\frac{\hbar^2}{2m}}}a \quad (4.57)$$

$$T = 16(1-\varepsilon)\varepsilon e^{-2\gamma\sqrt{1-\varepsilon}} = 16\left(1 - \frac{E}{V_0}\right)\frac{E}{V_0}e^{-a/\xi} \quad (4.58)$$

with characteristic length

$$\xi = \frac{1}{4}\sqrt{\frac{\hbar^2}{2m}/(V_0 - E)} \quad (4.59)$$

Finally we can use our results to analyze the situation where the potential is attractive instead of repulsive:

$$V(x) = \begin{cases} 0 & x < -a \\ -W_0 & -a \leq x \leq a \\ 0 & a < x \end{cases} \quad (4.60)$$

with $W_0 > 0$. In this case we obviously have only oscillatory solutions of the kind

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < -a \\ Ce^{ik'x} + De^{-ik'x} & -a \leq x \leq a \\ Fe^{ikx} & a < x \end{cases} \quad (4.61)$$

and we can again use our earlier solution and substitute

$$V_0 = -W_0. \quad (4.62)$$

It follows for the reflection coefficient

$$\frac{1}{T} = 1 + \frac{1}{4}\frac{V_0^2}{E(E+V_0)}\sin^2(2k'a) \quad (4.63)$$

where now

$$k' = \frac{\sqrt{2m(E+W_0)}}{\hbar}. \quad (4.64)$$

Using dimensionless quantities $\varepsilon = \frac{E}{W_0}$ and $\frac{\gamma^2}{4} = \frac{W_0}{\frac{\hbar^2}{2ma^2}}$ yields

$$T = \frac{1}{1 + \frac{\sin^2(\gamma\sqrt{\varepsilon+1})}{4\varepsilon(\varepsilon+1)}} \quad (4.65)$$

Again there are energy values where the barrier is fully transparent (if $\sin^2(2k'a) = 0$) a phenomenon called Ramsauer effect. Most striking is however the fact that even an attractive potential leads to a reflection and thus a reduced transmission of the incoming wave.

4.2 Bound and extended states

4.2.1 Rectangular box

We consider the same potential as in the above scattering problem:

$$V(x) = \begin{cases} V_0 & x < -a \\ 0 & -a \leq x \leq a \\ V_0 & a < x \end{cases} \quad (4.66)$$

only shifted by a constant such that $V(x) = 0$ in the center. In distinction to the situation of an incoming potential entering from one side, we are now only interested in the analysis of the solutions of the stationary Schrödinger equation. Then we can use the fact that for a potential

$$V(x) = V(-x) \quad (4.67)$$

follows that the wave function behaves as

$$\psi(x) = \pm\psi(-x). \quad (4.68)$$

The latter occurred already in the solution of the infinite potential well as well as for the harmonic oscillator. It can be generally seen from the following argument: Introduce the parity operator

$$\widehat{P}\psi(x) = \psi(-x). \quad (4.69)$$

It is an Hermitian operator

$$\begin{aligned} \int dx \psi(x)^* \widehat{P}\psi(x) &= \int dx \psi(x)^* \psi(-x) \\ &= \int dx \psi(-x)^* \psi(x) \\ &= \int dx (\widehat{P}\psi(x))^* \psi(x). \end{aligned} \quad (4.70)$$

It also commutes with a Hamiltonian with $V(x) = V(-x)$

$$\begin{aligned}\widehat{P}\widehat{H}\psi(x) &= \widehat{P}\left(\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x) \\ &= \left(\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(-x)\right)\widehat{P}\psi(x) \\ &= \widehat{H}\widehat{P}\psi(x)\end{aligned}\tag{4.71}$$

Thus \widehat{H} and \widehat{P} share the same eigenfunctions. It holds

$$\widehat{P}^2\psi(x) = \widehat{P}\psi(-x) = \psi(x)\tag{4.72}$$

The eigenvalues of \widehat{P}^2 are 1. Thus, the eigenvalues of \widehat{P} are ± 1 . Thus, the eigenfunctions of the Hamiltonian are either even or odd.

If $E > V_0$, it holds

$$\psi(x) = \begin{cases} Ae^{ik'x} + Be^{-ik'x} & x < -a \\ Ce^{ikx} + De^{-ikx} & -a \leq x \leq a \\ Ee^{ik'x} + Fe^{-ik'x} & a < x \end{cases}\tag{4.73}$$

with

$$\begin{aligned}k &= \frac{\sqrt{2mE}}{\hbar} \\ k' &= \frac{\sqrt{2m(E - V_0)}}{\hbar}.\end{aligned}\tag{4.74}$$

The fact that $\psi(x) = \pm\psi(-x)$ yields $E = \pm B$, $F = \pm A$ and $D = \pm C$. Even though there are two boundaries, the assumed reflection symmetry implies that it is sufficient to analyze only one. Doing so eliminates two of the three remaining constants. The final constant is being determined by the condition that the wave function is normalized inside some large volume $L \gg a$. We could proceed and do this analysis, but not much of interest happens. The key issue is that for $E > V_0$ a continuum of states (strictly a continuum only for $L \rightarrow \infty$) occurs.

It is more interesting to analyze $E < V_0$. In this case we have either

$$\psi(x) = \begin{cases} Ae^{\kappa'x} & x < -a \\ C \cos kx & -a \leq x \leq a \\ Ae^{-\kappa'x} & a < x \end{cases}\tag{4.75}$$

for even wave functions or

$$\psi(x) = \begin{cases} Ae^{\kappa x} & x < -a \\ C \sin kx & -a \leq x \leq a \\ -Ae^{-\kappa x} & a < x \end{cases}\tag{4.76}$$

for odd wave functions. Here we introduced

$$\begin{aligned}k &= \frac{\sqrt{2mE}}{\hbar} \\ \kappa &= \frac{\sqrt{2m(V_0 - E)}}{\hbar}.\end{aligned}\tag{4.77}$$

We first analyze even functions. It holds

$$\begin{aligned} e^{-\kappa a} &= \frac{C}{A} \cos ka \\ \kappa e^{-\kappa' a} &= k \frac{C}{A} \sin ka \end{aligned} \quad (4.78)$$

Thus

$$\kappa = k \tan ka \quad (4.79)$$

In case of odd wave functions follows

$$\begin{aligned} -e^{-\kappa a} &= \frac{C}{A} \sin ka \\ \kappa e^{-\kappa a} &= k \frac{C}{A} \cos ka \end{aligned} \quad (4.80)$$

which yields

$$\kappa = -k \cot ka \quad (4.81)$$

For convenience we introduce dimensionless quantities

$$\begin{aligned} \xi &= ka \\ \eta &= \kappa a \end{aligned} \quad (4.82)$$

Since k and κ both depend on energy we find

$$\begin{aligned} \xi^2 + \eta^2 &= a^2 \left(\frac{2mE}{\hbar^2} + \frac{2m(V_0 - E)}{\hbar^2} \right) \\ &= \frac{V_0}{\frac{\hbar^2}{2ma^2}} \equiv \gamma^2 \end{aligned} \quad (4.83)$$

Given the potential strength and width, we know γ . The above equation is determines a circle of radius γ . Since we know that $\xi > 0$ and $\kappa > 0$ we are only interested in the upper right quarter of the radius. In addition to Eq.4.83 we also need to solve

$$\eta = \begin{cases} \xi \tan \xi & \text{if } \psi(x) = +\psi(-x) \\ -\xi \cot \xi & \text{if } \psi(x) = -\psi(-x) \end{cases} \quad (4.84)$$

For $\gamma < \frac{\pi}{2}$ only one solution exists as $\cot \xi < 0$ only for $\xi > \frac{\pi}{2}$. Thus for

$$V_0 < \left(\frac{\pi}{2} \right)^2 \frac{\hbar^2}{2ma^2} \quad (4.85)$$

only one bound state exists that is even. For $\frac{\pi}{2} < \gamma < \pi$ we have one additional bound state that is odd. For $\gamma < m\frac{\pi}{2}$, corresponding to

$$V_0 < \left(m\frac{\pi}{2} \right)^2 \frac{\hbar^2}{2ma^2} \quad (4.86)$$

we have a total of m bound states. Obviously for $\gamma \rightarrow \infty$ all states are bound states. In this limit we know the eigenvalues

$$E_n^\infty = \left(\frac{n\pi}{2}\right)^2 \frac{\hbar^2}{2ma^2} \quad (4.87)$$

Thus, our condition for the existence of bound states is essentially that bound states disappear if

$$E_n^\infty > V_0. \quad (4.88)$$

One can also eliminate the variable η as follows:

$$\xi^2 + \eta^2 = \xi^2 (1 + \tan^2 \xi) = \frac{\xi^2}{\cos^2 \xi} \quad (4.89)$$

or

$$\xi^2 + \eta^2 = \xi^2 (1 + \cot^2 \xi) = \frac{\xi^2}{\sin^2 \xi} \quad (4.90)$$

Thus, it must hold

$$\xi = \begin{cases} \gamma \cos \xi & \text{if } \psi(x) = +\psi(-x) \\ \gamma \sin \xi & \text{if } \psi(x) = -\psi(-x) \end{cases} \quad (4.91)$$

and the roots of this equation determine the eigenvalues (one must however keep in mind to only accept solutions with $\cot \xi < 0$ in case of odd functions and $\tan \xi > 0$ in case of even functions).

In the limit $\gamma \ll 1$, where we have only one bound state we have to solve.

$$\xi = \gamma \cos \xi \quad (4.92)$$

for small γ . Thus, we expect a solution for very small ξ . We expand the cosine

$$\xi = \gamma \left(1 - \frac{1}{2}\xi^2\right) \quad (4.93)$$

which is solved for

$$\xi = \frac{\sqrt{1 + 2\gamma^2} - 1}{\gamma} \quad (4.94)$$

Expanding ξ^2 for small γ yields

$$\xi^2 \simeq \gamma^2 - \gamma^4 \quad (4.95)$$

which we can insert to obtain the eigenvalue of the single bound state:

$$E_0 = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \xi^2}{2ma^2} = V_0 - \frac{2ma^2}{\hbar^2} V_0^2. \quad (4.96)$$

Chapter 5

Angular momentum and spin

5.1 Particle on a circular orbit

Before we start to develop the formal apparatus of the angular momentum theory we analyze a simple problem, the motion of a particle on a circular orbit. We start from the classical Lagrange function

$$L(\varphi, \dot{\varphi}) = \frac{mR^2}{2} \dot{\varphi}^2 - V(\varphi), \quad (5.1)$$

with radius R of the orbit. The canonical momentum conjugated to φ is:

$$p_\varphi = \frac{\partial L(\varphi, \dot{\varphi})}{\partial \dot{\varphi}} = mR^2 \dot{\varphi} \quad (5.2)$$

such that the classical Hamiltonian function is

$$H(p_\varphi, \varphi) = \frac{p_\varphi^2}{2mR^2} + V(\varphi) \quad (5.3)$$

Using the quantization rules:

$$\begin{aligned} V(\varphi) &\rightarrow V(\varphi) \\ p_\varphi &\rightarrow \frac{\hbar}{i} \frac{\partial}{\partial \varphi} \end{aligned} \quad (5.4)$$

gives the Hamilton operator

$$H = -\frac{\hbar^2}{2mR^2} \frac{\partial^2}{\partial \varphi^2} + V(\varphi). \quad (5.5)$$

Take a system without potential gives the Schrödinger equation

$$-\frac{\hbar^2}{2mR^2} \frac{\partial^2}{\partial \varphi^2} \psi(\varphi) = E\psi(\varphi). \quad (5.6)$$

Since we consider a motion on a ring, we must obey the boundary condition

$$\psi(\varphi + 2\pi) = \psi(\varphi). \quad (5.7)$$

The solution is

$$\psi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}. \quad (5.8)$$

The boundary condition implies that

$$1 = e^{im2\pi}, \quad (5.9)$$

i.e. m is an integer. The eigenvalues of the momentum p_φ conjugated to φ are $\hbar m$. The energy eigenvalues are:

$$E_m = \frac{\hbar^2}{2mR^2} m^2. \quad (5.10)$$

The same result can be obtained if one writes the Laplace operator in spherical coordinates

$$\begin{aligned} x &= x_1 = r \cos \varphi \sin \theta \\ y &= x_2 = r \sin \varphi \sin \theta \\ z &= x_3 = r \cos \theta \end{aligned} \quad (5.11)$$

The Laplacian, $\nabla^2 = \sum_\alpha \frac{\partial^2}{\partial x_\alpha^2}$, in spherical coordinates is

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \quad (5.12)$$

The motion on a ring can be understood by fixing $r = R$ and $\theta = \frac{\pi}{2}$. Then

$$\nabla^2 = \frac{1}{R^2} \frac{\partial^2}{\partial \varphi^2} \quad (5.13)$$

and we obtain the above Hamiltonian.

5.2 angular momentum operator

Classically the angular momentum operator is

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (5.14)$$

In component notation this is

$$L_\alpha = \varepsilon_{\alpha\beta\gamma} x_\beta p_\gamma \quad (5.15)$$

where we sum over indices that occur twice. Since the momentum and position operators do not commute one might be afraid that $\mathbf{r} \times \mathbf{p}$ and $-\mathbf{p} \times \mathbf{x}$ are different. However writing the components explicitly gives

$$\begin{aligned} L_x &= yp_z - zp_y \\ L_y &= zp_x - xp_z \\ L_z &= xp_y - yp_x. \end{aligned} \quad (5.16)$$

The order of the operators obviously does not matter. Thus

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad (5.17)$$

and similar for the other components. In vector notation this can be written as

$$\hat{\mathbf{L}} = -i\hbar \mathbf{r} \times \nabla. \quad (5.18)$$

Similar to classical mechanics, we can establish a relation between the invariance of a physical system with respect to rotations. Consider a rotation of the coordinates by an infinitesimal angle $\delta\phi$ around an axis along the direction $\delta\phi$:

$$\mathbf{r} \rightarrow \mathbf{r} + \delta\mathbf{r} \quad (5.19)$$

with

$$\delta\mathbf{r} = \delta\phi \times \mathbf{r}. \quad (5.20)$$

The wave function in the new coordinates can be expanded:

$$\begin{aligned} \psi(\mathbf{r} + \delta\mathbf{r}) &\simeq \psi(\mathbf{r}) + \delta\mathbf{r} \cdot \nabla \psi(\mathbf{r}) \\ &= \psi(\mathbf{r}) + (\delta\phi \times \mathbf{r}) \cdot \nabla \psi(\mathbf{r}) \\ &= (1 + \delta\phi \cdot (\mathbf{r} \times \nabla)) \psi(\mathbf{r}) \end{aligned} \quad (5.21)$$

The last step follows from $(\delta\phi \times \mathbf{r}) \cdot \nabla = \varepsilon_{\alpha\beta\gamma} \delta\phi_\alpha x_\beta \partial_\gamma$. Thus

$$1 + \delta\phi \cdot (\mathbf{r} \times \nabla) \quad (5.22)$$

is the operator of infinitesimal rotations. If the Hamiltonian is invariant with respect to rotations it must hold $[(\mathbf{r} \times \nabla), \hat{H}] = 0$, which obviously corresponds to

$$[\hat{\mathbf{L}}, \hat{H}] = 0. \quad (5.23)$$

The angular momentum is conserved (remember we showed that it holds in general $i\hbar \frac{\partial}{\partial t} \langle \hat{A} \rangle_t = \langle [\hat{A}, \hat{H}] \rangle_t$) and can be measured sharply in the eigenstates of the Hamiltonian.

Using $[\hat{x}_\alpha, \hat{p}_\beta] = i\hbar \delta_{\alpha\beta}$ gives

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= (y\hat{p}_z - z\hat{p}_y)(z\hat{p}_x - x\hat{p}_z) - (z\hat{p}_x - x\hat{p}_z)(y\hat{p}_z - z\hat{p}_y) \\ &= y\hat{p}_x(\hat{p}_z z - z\hat{p}_z) + x\hat{p}_y(z\hat{p}_z - \hat{p}_z z) \\ &= i\hbar(x\hat{p}_y - y\hat{p}_x) = i\hbar \hat{L}_z \end{aligned} \quad (5.24)$$

In similar fashion follows

$$\begin{aligned} [\hat{L}_y, \hat{L}_z] &= i\hbar\hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar\hat{L}_y \end{aligned} \quad (5.25)$$

or generally:

$$[\hat{L}_\alpha, \hat{L}_\beta] = i\hbar\varepsilon_{\alpha\beta\gamma}\hat{L}_\gamma. \quad (5.26)$$

An interesting consequence of these commutation relation is that the magnitude of the angular momentum operator

$$\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \quad (5.27)$$

commutes with its components. It holds:

$$[L_z, \mathbf{L}^2] = [L_z, L_x^2] + [L_z, L_y^2].$$

The first term gives

$$\begin{aligned} [L_z, L_x^2] &= L_z L_x L_x - L_x L_x L_z \\ &= L_x L_z L_x + i\hbar L_y L_x - L_x L_x L_z \\ &= i\hbar(L_y L_x + L_x L_y), \end{aligned} \quad (5.28)$$

while the second one leads to

$$\begin{aligned} [L_z, L_y^2] &= L_z L_y L_y - L_y L_y L_z \\ &= L_y L_z L_y - i\hbar L_x L_y - L_y L_y L_z \\ &= -i\hbar(L_y L_x + L_x L_y). \end{aligned} \quad (5.29)$$

Thus, it holds

$$[L_z, \mathbf{L}^2] = 0 \quad (5.30)$$

and in a similar fashion follows for all components:

$$[L_\alpha, \mathbf{L}^2] = 0. \quad (5.31)$$

Thus, the components of \mathbf{L} have simultaneous eigenfunctions with \mathbf{L}^2 . On the other hand, the individual components do not have common eigenstates.

The last statement sounds paradox at first. The situation is however resolved if we take into account that all relevant states with nontrivial angular momentum are degenerate. We first analyze the expectation values

$$\langle L_\alpha \rangle = -i\hbar\varepsilon_{\alpha\beta\gamma} \int d^3r \psi^*(\mathbf{r}) x_\beta \frac{\partial}{\partial x_\gamma} \psi(\mathbf{r}). \quad (5.32)$$

It holds that $\langle L_\alpha \rangle$ vanishes for non-degenerate eigenvalues. To proof this statement we proceed as follows: First, if $\psi(\mathbf{r})$ is real (we ignore overall phase factors) then

$$\langle L_\alpha \rangle = i \times \text{real number}. \quad (5.33)$$

However $\langle L_\alpha \rangle$ must be real itself since it is Hermitian. Thus if $\psi(\mathbf{r})$ is real it holds $\langle L_\alpha \rangle = 0$. Next, we show that the wave function of a non-degenerate state is real. The stationary Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right) \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (5.34)$$

is purely real. If $\psi(\mathbf{r})$ is a solution then $\psi^*(\mathbf{r})$ is also a solution with same eigenvalue. Since by assumption our wave function is non-degenerate, $\psi(\mathbf{r})$ and $\psi^*(\mathbf{r})$ are the same function, i.e. the wave function of a non-degenerate state is real.

A related issue is the following: If we have two operators \hat{F} and \hat{G} that both commute with the Hamiltonian but that don't commute with each other the spectrum must be degenerate. Assume ψ is a state where in addition to the energy E the quantity F can be measured sharply. Then

$$\hat{G}\psi \neq \psi \quad (5.35)$$

since otherwise the \hat{F} and \hat{G} could be determined simultaneously. However

$$\hat{H}\hat{G}\psi = \hat{G}\hat{H}\psi = E\hat{G}\psi. \quad (5.36)$$

Thus, indeed, $\hat{G}\psi$ is degenerate with ψ but is not identical.

Thus we conclude that for a set of functions φ_m that are eigenvalues of, say \hat{L}_z

$$\hat{L}_z\varphi_m = \hbar m\varphi_m \quad (5.37)$$

holds that

$$\hat{L}_x\varphi_m \neq \varphi_m \quad \text{and} \quad \hat{L}_y\varphi_m \neq \varphi_m. \quad (5.38)$$

In case of a spherically symmetric potential hold however that φ_m , $\hat{L}_x\varphi_m$, and $\hat{L}_y\varphi_m$ are all degenerate. Thus, if there is an eigenstate of the Hamiltonian in which we can measure one component of the angular momentum sharply, we cannot measure in that same state the others sharply. On the other hand, we can construct linear combinations of those degenerate functions and in this state another component of \mathbf{L} can be measured sharply while the one we could previously determine is not sharply defined anymore.

5.3 General properties of angular momentum operators

In what follows we will analyze the properties of operators \hat{J}_α that obey the angular momentum algebra

$$[\hat{J}_\alpha, \hat{J}_\beta] = i\hbar\varepsilon_{\alpha\beta\gamma}\hat{J}_\gamma. \quad (5.39)$$

We use a new symbol \widehat{J}_α to express that these operators do not have to be identical to $-i\hbar\mathbf{r} \times \nabla$. We already showed that

$$\left[\widehat{J}_\alpha, \widehat{\mathbf{J}}^2\right] = 0 \quad (5.40)$$

as we only used the commutation relation of the type of Eq.5.39 to prove this result.

It is convenient to define

$$\widehat{J}_\pm = \widehat{J}_x \pm i\widehat{J}_y \quad (5.41)$$

and it obviously holds that $J_+ = J_-^\dagger$. Some immediate properties of these operators are

$$\begin{aligned} \left[\widehat{J}_z, \widehat{J}_\pm\right] &= \pm\hbar\widehat{J}_\pm \\ \left[\widehat{J}_\pm, \widehat{\mathbf{J}}^2\right] &= 0 \end{aligned} \quad (5.42)$$

It also follows

$$[J_+, J_-] = 2\hbar J_z \quad (5.43)$$

as well as

$$\begin{aligned} \widehat{\mathbf{J}}^2 &= J_- J_+ + J_z^2 + \hbar J_z \\ &= J_+ J_- + J_z^2 - \hbar J_z. \end{aligned} \quad (5.44)$$

We construct now the eigenfunctions of these operators.

Let

$$J_z \varphi_m = \hbar m \varphi_m \quad (5.45)$$

be the eigenfunctions of J_z with eigenvalue $\hbar m$. It holds

$$J_z J_+ \varphi_m = (\hbar J_+ + J_+ J_z) \varphi_m = \hbar(m+1) J_+ \varphi_m \quad (5.46)$$

Thus, $J_+ \varphi_m$ is an (un-normalized) eigenfunction of J_z with eigenvalue $\hbar(m+1)$.

$$J_+ \varphi_m = \alpha_m \varphi_{m+1}. \quad (5.47)$$

where α_m is a constant pre-factor that guarantees normalization.

Applying J_+ again gives

$$J_+^2 \varphi_m = \alpha_m J_+ \varphi_{m+1} = \alpha_m \alpha_{m+1} \varphi_{m+2}. \quad (5.48)$$

In a similar fashion we obtain

$$J_- \varphi_m = \alpha'_m \varphi_{m-1} \quad (5.49)$$

etc. and we have found a scheme of generating a sequence of eigenfunctions from one eigenfunction.

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Since $\widehat{\mathbf{J}}^2$ commutes with J_z , they have common eigenfunctions

$$\widehat{\mathbf{J}}^2 \varphi_m = \hbar^2 K_m^2 \varphi_m. \quad (5.50)$$

Since $\widehat{\mathbf{J}}^2$ also commutes with J_{\pm} it follows

$$\begin{aligned} \widehat{\mathbf{J}}^2 \varphi_{m+1} &= \frac{1}{\alpha_m} \widehat{\mathbf{J}}^2 J_+ \varphi_m = J_+ \widehat{\mathbf{J}}^2 \varphi_m \\ &= \frac{1}{\alpha_m} \hbar^2 K_m^2 J_+ \varphi_m = \hbar^2 K_m^2 \varphi_{m+1} \end{aligned} \quad (5.51)$$

But it also holds

$$\widehat{\mathbf{J}}^2 \varphi_{m+1} = \hbar^2 K_{m+1}^2 \varphi_{m+1} \quad (5.52)$$

implying $K_m^2 = K_{m+1}^2$.

Equally we find $K_m^2 = K_{m-1}^2$. Since m is arbitrary it follows that K^2 is independent of m for all φ_m of the above sequence.

How many such eigenfunctions are there? It follows

$$\langle m | \widehat{\mathbf{J}}^2 | m \rangle = \hbar^2 K^2 = \langle m | \widehat{J}_x^2 | m \rangle + \langle m | \widehat{J}_y^2 | m \rangle + \hbar^2 m^2 \quad (5.53)$$

which implies

$$K^2 \geq m^2 \quad (5.54)$$

Thus, for a given value $K > 0$, the possible values of m fall between $-K$ and K . We can always assume $K > 0$ as only K^2 is relevant. If m_{\max} is the maximal value of m for given K , then

$$J_+ \varphi_{m_{\max}} = 0 \quad (5.55)$$

and similarly

$$J_- \varphi_{m_{\min}} = 0. \quad (5.56)$$

Using the above result for $\widehat{\mathbf{J}}^2$ and the last two equations, one obtains

$$\begin{aligned} \widehat{\mathbf{J}}^2 &= J_- J_+ + J_z^2 + \hbar J_z \\ &= J_+ J_- + J_z^2 - \hbar J_z. \end{aligned} \quad (5.57)$$

$$\widehat{\mathbf{J}}^2 \varphi_{m_{\max}} = \hbar^2 K^2 \varphi_{m_{\max}} = \hbar^2 m_{\max} (m_{\max} + 1) \varphi_{m_{\max}} \quad (5.58)$$

as well as

$$\widehat{\mathbf{J}}^2 \varphi_{m_{\min}} = \hbar^2 K^2 \varphi_{m_{\min}} = \hbar^2 m_{\min} (m_{\min} - 1) \varphi_{m_{\min}} \quad (5.59)$$

and it follows

$$m_{\max} (m_{\max} + 1) = m_{\min} (m_{\min} - 1) \quad (5.60)$$

This quadratic equation for m_{\max} has two solutions

$$\begin{aligned} m_{\max} &= -m_{\min} \\ m_{\max} &= m_{\min} - 1 \end{aligned} \quad (5.61)$$

The last one is obviously not allowed as by construction $m_{\max} \geq m_{\min}$. The possible values form therefore a symmetric sequence about $m = 0$. Let us call

$$m_{\max} = j \quad (5.62)$$

then m runs from $-j$ to j in unit steps. Thus, it follows

$$j = \begin{cases} \text{integer} & \text{if } m = 0 \text{ is included} \\ \frac{1}{2} \times \text{odd integer} & \text{if } m = 0 \text{ is not included} \end{cases} \quad (5.63)$$

Draw picture for $j = 2$ and $j = \frac{3}{2}$. It also follows that m is an integer if j is and that m is an odd multiple of $\frac{1}{2}$ if j is $\frac{1}{2} \times \text{odd integer}$. In either case follows

$$\begin{aligned} \widehat{\mathbf{J}}^2 \varphi_{j,m} &= \hbar^2 j(j+1) \varphi_{j,m} \\ J_z \varphi_{j,m} &= \hbar m \varphi_{j,m} \quad \text{with } m_j = -j, \dots, j \end{aligned} \quad (5.64)$$

We can also determine the coefficients α_m and α'_m that occur if we apply J_{\pm} :

$$\begin{aligned} J_+ |m\rangle &= \alpha_m |m+1\rangle \\ J_- |m\rangle &= \alpha'_m |m-1\rangle \end{aligned} \quad (5.65)$$

To determine α_m we evaluate the norm of $J_+ |m\rangle$ as

$$\begin{aligned} |\alpha_m|^2 &= \langle m | J_- J_+ | m \rangle = \langle m | \widehat{\mathbf{J}}^2 - J_z^2 - \hbar J_z | m \rangle \\ &= \hbar^2 [j(j+1) - m^2 + m] \langle m | m \rangle \end{aligned} \quad (5.66)$$

Which yields

$$\alpha_m = \hbar \sqrt{j(j+1) - m(m+1)} \quad (5.67)$$

Similarly we obtain

$$\alpha'_m = \hbar \sqrt{j(j+1) - m(m-1)} \quad (5.68)$$

Thus, it holds

$$J_{\pm} \varphi_{j,m} = \hbar \sqrt{j(j+1) - m(m \pm 1)} \varphi_{j,m \pm 1} \quad (5.69)$$

which obey immediately that $J_+ \varphi_{m_{\max}} = 0$ and $J_- \varphi_{m_{\min}} = 0$.

5.4 Eigenfunctions of the angular momentum

First, we determine the angular momentum in spherical coordinates. For example in case of the z -component holds

$$\widehat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad (5.70)$$

To determine \widehat{L}_z we use holds the following:

$$\frac{\partial}{\partial y} = \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial y} \frac{\partial}{\partial \varphi} + \frac{\partial r}{\partial y} \frac{\partial}{\partial r} \quad (5.71)$$

and similar for $\frac{\partial}{\partial x}$. Using the following relation for spherical coordinates

$$\begin{aligned} r^2 &= x^2 + y^2 + z^2 \\ \cos \theta &= \frac{z}{r} \\ \tan \phi &= \frac{y}{x} \end{aligned} \quad (5.72)$$

gives

$$\frac{\partial r}{\partial x} = \frac{x}{r} \quad \text{and} \quad \frac{\partial r}{\partial y} = \frac{y}{r}. \quad (5.73)$$

Alternatively we can analyze:

$$\begin{aligned} -\sin \theta \frac{\partial \theta}{\partial x} &= \frac{\partial}{\partial x} \cos \theta = z \frac{\partial}{\partial x} \frac{1}{r} \\ &= -\frac{zx}{r^3} = -\frac{\cos \varphi \sin \theta \cos \theta}{r} \end{aligned} \quad (5.74)$$

This leads to:

$$\frac{\partial \theta}{\partial x} = \frac{\cos \varphi \cos \theta}{r}. \quad (5.75)$$

Other derivatives can be analyzed along the same fashion and it follows

$$\begin{aligned} \widehat{L}_x &= i\hbar \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \\ \widehat{L}_z &= i\hbar \left(-\cos \varphi \frac{\partial}{\partial \theta} + \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \\ \widehat{L}_z &= -i\hbar \frac{\partial}{\partial \varphi} \end{aligned} \quad (5.76)$$

Thus, our particle on a circular orbit has an Hamiltonian

$$H_{\text{circ}} = \frac{\hbar^2}{2mR^2} \widehat{L}_z^2 + V(\varphi) \quad (5.77)$$

This suggests to analyze

$$\widehat{\mathbf{L}}^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \quad (5.78)$$

and with our earlier form of the Laplace operator in spherical coordinates follows

$$H = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{2mr^2} + V(\mathbf{r}). \quad (5.79)$$

If one introduces

$$\hat{p}_r = -i\hbar \frac{1}{r} \frac{\partial}{\partial r} r \quad (5.80)$$

the Hamiltonian can also be written as:

$$H = \frac{1}{2m} \left(\hat{p}_r^2 + \frac{\hat{\mathbf{L}}^2}{r^2} \right) + V(\mathbf{r}). \quad (5.81)$$

The last results make explicit that for

$$V(\mathbf{r}) = V(r) \quad (5.82)$$

holds that $[\mathbf{L}, H] = 0$.

Next we determine the eigenfunctions of the operators L_α . We write

$$L_z Y_{l,m}(\theta, \varphi) = \hbar m Y_{l,m}(\theta, \varphi) \quad (5.83)$$

where $m = -l, \dots, l$. In spherical coordinates holds

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi} \quad (5.84)$$

and we find

$$\frac{\partial}{\partial \varphi} Y_{l,m}(\theta, \varphi) = im Y_{l,m}(\theta, \varphi). \quad (5.85)$$

This equation determines only the φ part. If we set

$$Y_{l,m}(\theta, \varphi) = \Phi_m(\varphi) \Theta_{lm}(\theta) \quad (5.86)$$

it follows

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \quad (5.87)$$

which is normalized according to

$$\int_0^{2\pi} d\varphi |\Phi_m(\varphi)|^2 = 1. \quad (5.88)$$

The index m can be determined from the single valuedness of Φ

$$\Phi(\varphi) = \Phi(\varphi + 2\pi) \quad (5.89)$$

which yields that m is an integer. From our above analysis follows immediately that l must also be an integer. We therefore obtain

$$Y_{l,m}(\theta, \varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \Theta_{lm}(\theta). \quad (5.90)$$

Using the results for the angular momentum in spherical coordinates gives

$$\begin{aligned} \hat{L}_+ &= \hat{L}_x + i\hat{L}_y = \hbar e^{i\varphi} \left(i \cot \theta \frac{\partial}{\partial \varphi} + \frac{\partial}{\partial \theta} \right) \\ \hat{L}_- &= \hat{L}_x - i\hat{L}_y = \hbar e^{-i\varphi} \left(i \cot \theta \frac{\partial}{\partial \varphi} - \frac{\partial}{\partial \theta} \right) \end{aligned} \quad (5.91)$$

Since $l = m_{\max}$ it must hold

$$\widehat{L}_+ Y_{l,l}(\theta, \varphi) = 0 \quad (5.92)$$

which gives

$$e^{i\varphi} \left(i \cot \theta \frac{\partial}{\partial \varphi} + \frac{\partial}{\partial \theta} \right) e^{il\varphi} \Theta_{l,l}(\theta) = 0 \quad (5.93)$$

evaluating the derivative w.r.t φ gives

$$\left(-l \cot \theta + \frac{\partial}{\partial \theta} \right) \Theta_{l,l}(\theta) = 0 \quad (5.94)$$

which is identical to

$$\frac{\partial \Theta_{l,l}}{\partial \theta} = l \cot \theta \Theta_{l,l} \quad (5.95)$$

Using the identity

$$l \cot \theta = \frac{\partial}{\partial \theta} \log \sin^l \theta \quad (5.96)$$

we can write

$$\frac{1}{\Theta_{l,l}} \frac{\partial \Theta_{l,l}}{\partial \theta} = \frac{\partial \log \Theta_{l,l}}{\partial \theta} = \frac{\partial}{\partial \theta} \log \sin^l \theta \quad (5.97)$$

This is simply integrated to yield

$$\Theta_{l,l} = C \sin^l \theta \quad (5.98)$$

Including the normalization factor yields

$$Y_{l,l}(\theta, \varphi) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}} \sin^l \theta e^{il\varphi} \quad (5.99)$$

where the sign factor $(-1)^l$ is convention.

Similarly it follows from

$$\widehat{L}_- Y_{l,-l}(\theta, \varphi) = 0 \quad (5.100)$$

that

$$Y_{l,-l}(\theta, \varphi) = \frac{1}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}} \sin^l \theta e^{-il\varphi}. \quad (5.101)$$

Other values for $Y_{l,m}(\theta, \varphi)$ can be obtained from by applying \widehat{L}_+ to $Y_{l,-l}(\theta, \varphi)$:

$$\begin{aligned} Y_{l,-l+1}(\theta, \varphi) &= \frac{\widehat{L}_+ Y_{l,-l}(\theta, \varphi)}{\hbar \sqrt{2(2l-1)}} \\ &= \frac{e^{i\varphi}}{\sqrt{2(2l-1)}} \left(i \cot \theta \frac{\partial}{\partial \varphi} + \frac{\partial}{\partial \theta} \right) \frac{1}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}} \sin^l \theta e^{-il\varphi} \\ &= \sqrt{\frac{(2l+1)!}{8\pi(2l-1)}} \frac{e^{i\varphi}}{2^l l!} \left(l \cot \theta + \frac{\partial}{\partial \theta} \right) \sin^l \theta e^{-il\varphi} \\ &= \sqrt{\frac{(2l+1)!}{8\pi(2l-1)}} \frac{2l}{2^l l!} \cos \theta \sin^{l-1} \theta e^{i(-l+1)\varphi} \end{aligned} \quad (5.102)$$

In general this can be written as

$$Y_{l,m}(\theta, \varphi) = (-1)^{\frac{m+|m|}{2}} \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos\theta) e^{im\varphi}. \quad (5.103)$$

with associated Legendre polynomials

$$P_l^m(\mu) = (1-\mu^2)^{m/2} \frac{d^m P_l(\mu)}{d\mu^m} \quad (5.104)$$

for $m \geq 0$ and Legendre polynomials

$$P_l(\mu) = \frac{1}{2^l l!} \frac{d^l}{d\mu^l} (\mu^2 - 1)^l. \quad (5.105)$$

It holds $P_l^{-m}(\mu) = P_l^m(\mu)$. The pre-factors are chosen to ensure that

$$\int d\Omega Y_{l,m}^*(\theta, \varphi) Y_{l',m'}(\theta, \varphi) = \delta_{ll'} \delta_{mm'} \quad (5.106)$$

where $\int d\Omega \dots = \int \sin\theta d\theta d\varphi \dots$

It holds

$$\begin{aligned} P_0(\mu) &= 1 \\ P_1(\mu) &= \mu \\ P_2(\mu) &= \frac{1}{2}(3\mu^2 - 1) \\ P_3(\mu) &= \frac{1}{2}(5\mu^3 - 3\mu) \end{aligned} \quad (5.107)$$

and in general it holds that

$$P_l(\mu) = (-1)^l P_l(-\mu). \quad (5.108)$$

This leads immediately to

$$P_l^m(\mu) = (-1)^{l-m} P_l^m(-\mu). \quad (5.109)$$

These results allow us to analyze the properties of $Y_{l,m}(\theta, \varphi)$ under the parity operation. For a vector on a sphere it holds that $\mathbf{r} \rightarrow -\mathbf{r}$ corresponds to

$$(\theta, \varphi) = (\pi - \theta, \varphi + \pi) \quad (5.110)$$

and the thus using $Y_{l,m}(\theta, \varphi) = C_{lm} P_l^m(\cos\theta) e^{im\varphi}$ gives

$$\begin{aligned} \mathcal{P}Y_{l,m}(\theta, \varphi) &= Y_{l,m}(\pi - \theta, \varphi + \pi) \\ &= C_{lm} P_l^m(-\cos\theta) e^{im\varphi} (-1)^m \\ &= (-1)^{l-m} (-1)^m C_{lm} P_l^m(\cos\theta) e^{im\varphi} \\ &= (-1)^l Y_{l,m}(\theta, \varphi). \end{aligned} \quad (5.111)$$

Thus, for l even is the parity of an angular momentum state 1 while it is -1 for l odd.

Also, since the P_l^m are purely real functions, it follows

$$Y_{l,-m}(\theta, \varphi) = (-1)^m Y_{l,m}^*(\theta, \varphi). \quad (5.112)$$

The explicit result for $l = m = 0$ is:

$$Y_{0,0} = \frac{1}{2\sqrt{\pi}} \quad (5.113)$$

For $l = 1$ follows:

$$\begin{aligned} Y_{1,-1} &= \frac{1}{2} e^{-i\phi} \sqrt{\frac{3}{2\pi}} \sin \theta \\ Y_{1,0} &= \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta \\ Y_{1,1} &= -\frac{1}{2} e^{i\phi} \sqrt{\frac{3}{2\pi}} \sin \theta \end{aligned} \quad (5.114)$$

For $l = 2$ holds instead.

$$\begin{aligned} Y_{2,-2} &= \frac{1}{4} e^{-2i\phi} \sqrt{\frac{15}{2\pi}} \sin^2 \theta \\ Y_{2,-1} &= \frac{1}{2} e^{-i\phi} \sqrt{\frac{15}{2\pi}} \cos \theta \sin \theta \\ Y_{2,0} &= \frac{1}{4} \sqrt{\frac{5}{\pi}} (3 \cos^2 \theta - 1) \\ Y_{2,1} &= \frac{-1}{2} e^{i\phi} \sqrt{\frac{15}{2\pi}} \cos \theta \sin \theta \\ Y_{2,2} &= \frac{1}{4} e^{2i\phi} \sqrt{\frac{15}{2\pi}} \sin^2 \theta \end{aligned} \quad (5.115)$$

Since the spherical harmonics build a complete set of functions, each function $f(\theta, \varphi)$ on the surface of a sphere can be expanded as

$$f(\theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l a_{l,m} Y_{l,m}(\theta, \varphi) \quad (5.116)$$

where

$$a_{lm} = \int d\Omega Y_{l,m}^*(\theta, \varphi) f(\theta, \varphi). \quad (5.117)$$

5.5 The spin

Electrons that are sent through an inhomogeneous magnetic field display a deflection in two subsets. This is the so called Stern–Gerlach experiment. It

clearly shows that there exists an internal degree of freedom that can naturally be captured by generalizing the wave function as

$$\psi(\mathbf{r}) \rightarrow \psi(\mathbf{r}, \sigma). \quad (5.118)$$

Since there are two values of the internal degree of freedom, we write $\sigma = \uparrow$ and \downarrow or $\sigma = \pm 1$. Often it is also useful to write the wave function as a *spinor*

$$\Psi(\mathbf{r}) = \begin{pmatrix} \psi_{\uparrow}(\mathbf{r}) \\ \psi_{\downarrow}(\mathbf{r}) \end{pmatrix}. \quad (5.119)$$

The coupling to the magnetic field suggests that this internal degree of freedom is an angular momentum. Thus, there is an operator \mathbf{s} with $[s_{\alpha}, s_{\beta}] = i\hbar\varepsilon_{\alpha\beta\gamma}s_{\gamma}$. The operator acts on a two dimensional Hilbert space and is thus a 2×2 matrix. This is accomplished by

$$s_{\alpha} = \frac{\hbar}{2}\sigma_{\alpha} \quad (5.120)$$

where σ_{α} are the Pauli matrices.

$$\begin{aligned} \sigma_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \sigma_y &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ \sigma_z &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned} \quad (5.121)$$

Gives

$$\hat{\mathbf{S}}^2 = \frac{3}{4}\hbar^2 = s(s+1)\hbar^2 \quad (5.122)$$

thus this is a spin $s = \frac{1}{2}$.

It is related to a magnetic moment

$$\boldsymbol{\mu} = -\gamma\mathbf{s} \quad (5.123)$$

where $\gamma \simeq \frac{e}{mc}$. Thus, assuming the equal sign, gives

$$\boldsymbol{\mu} = -\mu_B\boldsymbol{\sigma} \quad (5.124)$$

where $\mu_B = \frac{e\hbar}{2mc} = 9.2740154 \times 10^{-24}\text{JT}^{-1}$ is the Bohr magneton. In the case of an external magnetic field holds $V = -\boldsymbol{\mu} \cdot \mathbf{B}$ which gives rise to

$$H \rightarrow H + \gamma\mathbf{s} \cdot \mathbf{B} = H + \mu_B\boldsymbol{\sigma} \cdot \mathbf{B} \quad (5.125)$$

5.5.1 Precession of a spin in a magnetic field

Ignore the space dependence and consider only the spin degree of freedom

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad (5.126)$$

If the magnetic field points into the z -direction it follows

$$\hat{H} = \mu_B \boldsymbol{\sigma} \cdot \mathbf{B} = \mu_B B \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (5.127)$$

The eigenvalues of the Hamiltonian are immediately determined as

$$E_\sigma = \sigma \mu_B B = m_s \hbar \omega_L \quad (5.128)$$

where $\sigma = \pm 1$ or $m_s = \pm \frac{1}{2}$. Here

$$\omega_L = \frac{2\mu_B B}{\hbar} = \frac{eB}{mc} \quad (5.129)$$

is the Lamor frequency .

Thus, it follows

$$\begin{aligned} i\hbar \frac{\partial \psi_\uparrow}{\partial t} &= \mu_B B \psi_\uparrow \\ i\hbar \frac{\partial \psi_\downarrow}{\partial t} &= -\mu_B B \psi_\downarrow \end{aligned} \quad (5.130)$$

Which is readily solved as

$$\begin{aligned} \psi_\uparrow(t) &= \psi_\uparrow(0) e^{i\frac{\omega_L}{2}t} \\ \psi_\downarrow(t) &= \psi_\downarrow(0) e^{-i\frac{\omega_L}{2}t} \end{aligned} \quad (5.131)$$

We can for example analyze the expectation value

$$\begin{aligned} \langle s_x \rangle &= \Psi^* s_x \Psi = \frac{\hbar}{2} (\psi_\uparrow^*(t), \psi_\downarrow^*(t)) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_\uparrow(t) \\ \psi_\downarrow(t) \end{pmatrix} \\ &= \frac{\hbar}{2} (\psi_\uparrow^*(t) \psi_\downarrow(t) + \psi_\downarrow^*(t) \psi_\uparrow(t)) \\ &= \frac{\hbar}{2} (\psi_\uparrow^*(0) \psi_\downarrow(0) e^{-i\omega_L t} + \psi_\downarrow^*(0) \psi_\uparrow(0) e^{i\omega_L t}) \end{aligned} \quad (5.132)$$

Since

$$\psi_\uparrow^*(0) \psi_\uparrow(0) + \psi_\downarrow^*(0) \psi_\downarrow(0) = 1 \quad (5.133)$$

we can write

$$\begin{aligned} \psi_\uparrow(0) &= \cos \alpha e^{i\varphi} \\ \psi_\downarrow(0) &= \sin \alpha \end{aligned} \quad (5.134)$$

and it follows

$$\langle s_x \rangle = A \cos(\omega_L t + \varphi). \quad (5.135)$$

with $A = \hbar \cos \alpha \sin \alpha$. It follows similarly

$$\langle s_y \rangle = A \sin(\omega_L t + \varphi). \quad (5.136)$$

5.6 Addition of angular momentum

We consider a system of two particles moving on a sphere (also called two rotor system) with angular momentum \mathbf{L}_1 and \mathbf{L}_2 or of a particle with angular momentum \mathbf{L} and spin \mathbf{S} . In both cases we can describe the state of the system by the combined wave function

$$|l, m_l\rangle |s, m_s\rangle \quad (5.137)$$

or

$$|l_1, m_1\rangle |l_2, m_2\rangle. \quad (5.138)$$

However, the conserved quantity is in such situations often the total angular momentum

$$\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2 \quad (5.139)$$

or

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (5.140)$$

making it more appropriate to use a basis where the quantum numbers are those of \mathbf{L} or \mathbf{J} . To be specific, we analyze the case of the two rotor system.

We first need to identify the correct quantum numbers, i.e. quantum numbers that can be simultaneously determined. It is natural to chose

$$\begin{aligned} \mathbf{L}^2 &= (\mathbf{L}_1 + \mathbf{L}_2)^2 = \mathbf{L}_1^2 + \mathbf{L}_2^2 + 2\mathbf{L}_1 \cdot \mathbf{L}_2 \\ L_z &= L_{1,z} + L_{2,z} \end{aligned} \quad (5.141)$$

Furthermore it holds that

$$[\mathbf{L}_1^2, \mathbf{L}^2] = 2[\mathbf{L}_1^2, \mathbf{L}_1 \cdot \mathbf{L}_2] = 0 \quad (5.142)$$

and

$$[\mathbf{L}_1^2, L_z] = [\mathbf{L}_1^2, L_{1,z} + L_{2,z}] = [\mathbf{L}_1^2, L_{1,z}] = 0 \quad (5.143)$$

Thus, a complete set of quantum numbers is

$$|l, m, l_1 l_2\rangle \quad (5.144)$$

We need to know how one state can be expressed in terms of the other i.e.

$$|l, m, l_1 l_2\rangle = \sum_{m_1, m_2} |l_1, m_1\rangle |l_2, m_2\rangle \langle l, m, l_1 l_2 | l_1, m_1, l_2, m_2\rangle \quad (5.145)$$

Since $L_z = L_{1,z} + L_{2,z}$ it hold of course

$$m = m_1 + m_2 \quad (5.146)$$

and we have only one summation left. The coefficients

$$C_{m_1, m_2}^{l m l_1 l_2} = \langle l, m, l_1 l_2 | l_1, m_1, l_2, m_2\rangle \quad (5.147)$$

are called Clebsch-Gordan coefficients. The quantity

$$\left| C_{m_1, m_2}^{lm_1 l_2} \right|^2 \quad (5.148)$$

measures the probability that for two particles with total angular momentum l_1 and l_2 at fixed l and m the measurement finds one particle with $L_{1,z} = \hbar m_1$ and the other with $L_{2,z} = \hbar m_2$.

Example: We consider:

$$|l, m, l_1 l_2\rangle = |1, -1, 1, 1\rangle \quad (5.149)$$

Using $m_1 + m_2 = -1$ it follows

$$|1, -1, 1, 1\rangle = C_{0,-1} |1, 0\rangle |1, -1\rangle + C_{-1,0} |1, -1\rangle |1, 0\rangle \quad (5.150)$$

The coefficients are determined by normalization and application of L_{\pm} operators.

$$\begin{aligned} L_- |1, -1, 1, 1\rangle &= 0 \\ &= (L_{1-} + L_{2-}) C_{0,-1} |1, 0\rangle |1, -1\rangle \\ &\quad + (L_{1-} + L_{2-}) C_{-1,0} |1, -1\rangle |1, 0\rangle \end{aligned} \quad (5.151)$$

It holds

$$L_{1-} |1, 0\rangle_1 = \sqrt{2} |1, -1\rangle_1 \quad (5.152)$$

and similarly for the second particle. Thus

$$0 = \sqrt{2} (C_{0,-1} + C_{-1,0}) |1, -1\rangle |1, -1\rangle \quad (5.153)$$

which gives

$$C_{0,-1} = -C_{-1,0}. \quad (5.154)$$

Normalization gives $|C_{0,-1}|^2 = |C_{-1,0}|^2 = \frac{1}{2}$ such that

$$|1, -1, 1, 1\rangle = \frac{1}{\sqrt{2}} |1, 0\rangle |1, -1\rangle - \frac{1}{\sqrt{2}} |1, -1\rangle |1, 0\rangle \quad (5.155)$$

5.7 Interacting spins

As a simple toy model for interacting spins we consider two coupled spin- $\frac{1}{2}$ particles described by the Hamiltonian:

$$H = J \mathbf{s}_1 \cdot \mathbf{s}_2 + \gamma (\mathbf{s}_1 + \mathbf{s}_2) \cdot \mathbf{B} \quad (5.156)$$

Consider first $\mathbf{B} = \mathbf{0}$. If we consider the total spin

$$\begin{aligned} \mathbf{S} &= \mathbf{s}_1 + \mathbf{s}_2 \\ \mathbf{S}^2 &= \mathbf{s}_1^2 + \mathbf{s}_2^2 + 2\mathbf{s}_1 \cdot \mathbf{s}_2 \end{aligned} \quad (5.157)$$

we obtain immediately:

$$\mathbf{S}^2 = S(S+1)\hbar^2 \quad (5.158)$$

Either we have singlets or triplets $S = 0$ or $S = 1$. For the Hamiltonian follows

$$H = J\mathbf{s}_1 \cdot \mathbf{s}_2 = \frac{J\hbar^2}{2} \left(S(S+1) - \frac{3}{2} \right) \quad (5.159)$$

Thus, for $J > 0$ the ground state is a singlet

$$E_{S=0} = -\frac{3}{4}J\hbar^2 \quad (5.160)$$

and the excited states are degenerated triplet states

$$E_{S=1} = \frac{J\hbar^2}{4}. \quad (5.161)$$

If we add the magnetic field $\mathbf{B} = (0, 0, B)$ we obtain

$$E_{S,m} = \frac{J\hbar^2}{2} \left(S(S+1) - \frac{3}{2} \right) + m\gamma B\hbar \quad (5.162)$$

Thus, the singlet state as well as the $m = 0$ triplet are unaffected by the magnetic field, while the two $m = \pm 1$ triplet states are affected. There is a critical field B_c where the $m = -1$ triplet states becomes lower than the singlet

$$-\frac{3}{4}J\hbar^2 = \frac{J\hbar^2}{4} - \gamma B_c\hbar \quad (5.163)$$

which yields

$$B_c = \frac{J\hbar}{\gamma}. \quad (5.164)$$

Chapter 6

Particles in an external magnetic field

6.1 Gauge invariance

Classically a particle in an external electromagnetic field is characterized by the Hamiltonian

$$H = \frac{1}{2m} \left(\mathbf{p} - \frac{e}{c} \mathbf{A} \right)^2 + e\varphi \quad (6.1)$$

where \mathbf{A} is the vector potential and φ the scalar potential. They determine the magnetic and electric fields

$$\begin{aligned} \mathbf{B} &= \nabla \times \mathbf{A}, \\ \mathbf{E} &= \nabla\varphi + \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \end{aligned} \quad (6.2)$$

We know that the magnetic and electric fields are unaffected if there is a gauge transformation

$$\begin{aligned} \mathbf{A} &\rightarrow \mathbf{A}' = \mathbf{A} + \nabla f \\ \varphi &\rightarrow \varphi' = \varphi - \frac{1}{c} \frac{\partial f}{\partial t} \end{aligned} \quad (6.3)$$

In what follows we will quantize this theory. Write the corresponding Schrödinger equation

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \left(\frac{1}{2m} \left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}(\hat{\mathbf{r}}) \right)^2 + e\varphi(\hat{\mathbf{r}}) \right) \psi(\mathbf{r}, t). \quad (6.4)$$

Lets first analyze the consequences of a gauge transformation:

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \left(\frac{1}{2m} \left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}' + \frac{e}{c} \nabla f \right)^2 + e\varphi'(\hat{\mathbf{r}}) + \frac{e}{c} \frac{\partial f}{\partial t} \right) \psi(\mathbf{r}, t). \quad (6.5)$$

We introduce

$$\psi(\mathbf{r}, t) = \psi'(\mathbf{r}, t) e^{-i \frac{e}{\hbar c} f} \quad (6.6)$$

which gives

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \left(i\hbar \frac{\partial \psi'(\mathbf{r}, t)}{\partial t} + \frac{e}{c} \psi'(\mathbf{r}, t) \frac{\partial f(\mathbf{r}, t)}{\partial t} \right) e^{-i \frac{e}{\hbar c} f(\mathbf{r}, t)} \quad (6.7)$$

$$\hat{\mathbf{p}}\psi(\mathbf{r}, t) = \left(\hat{\mathbf{p}}\psi'(\mathbf{r}, t) - \frac{e}{c} \psi'(\mathbf{r}, t) \nabla f(\mathbf{r}, t) \right) e^{-i \frac{e}{\hbar c} f(\mathbf{r}, t)} \quad (6.8)$$

such that

$$\left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}' + \frac{e}{c} \nabla f(\mathbf{r}, t) \right) \psi(\mathbf{r}, t) = \left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}' \right) \psi'(\mathbf{r}, t) e^{-i \frac{e}{\hbar c} f(\mathbf{r}, t)} \quad (6.9)$$

and thus

$$\left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}' + \frac{e}{c} \nabla f(\mathbf{r}, t) \right)^2 \psi(\mathbf{r}, t) = \left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}' \right)^2 \psi'(\mathbf{r}, t) e^{-i \frac{e}{\hbar c} f(\mathbf{r}, t)} \quad (6.10)$$

Thus it follows

$$i\hbar \frac{\partial \psi'(\mathbf{r}, t)}{\partial t} = \left(\frac{1}{2m} \left(\left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}' \right)^2 \right) + e\varphi'(\mathbf{r}) \right) \psi'(\mathbf{r}, t) \quad (6.11)$$

The Schrödinger equation is therefore only invariant with respect to the gauge transformation of the electromagnetic potential if the wave function is simultaneously transformed as

$$\psi(\mathbf{r}, t) \rightarrow \psi'(\mathbf{r}, t) = \psi(\mathbf{r}, t) e^{i \frac{e}{\hbar c} f(\mathbf{r}, t)}. \quad (6.12)$$

The phase of the wave function is therefore related to the gauge function of the electromagnetic field.

When we discussed the continuity equation for the probability density we concluded that the gradient of the phase determines the probability current and is therefore measurable. This statement was however only correct for particles without magnetic field. Within a magnetic field the corresponding current density is given by

$$\mathbf{j} = \frac{\hbar}{2im} (\psi^* \nabla \psi - (\nabla \psi^*) \psi) - \frac{e}{mc} \mathbf{A} |\psi|^2 \quad (6.13)$$

which is gauge invariant.

6.2 Landau levels in a magnetic field

We consider non-interacting electrons in a homogeneous magnetic field

$$\mathbf{B} = (0, 0, B). \quad (6.14)$$

This can be generated from the vector potential

$$\mathbf{A} = (-By, 0, 0), \quad (6.15)$$

which leads to

$$H = \frac{1}{2m} \left(p_x + \frac{eB}{c} y \right)^2 + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \quad (6.16)$$

translation invariant w.r.t x and y coordinate. Thus

$$\psi(\mathbf{r}) = e^{i(k_x x + k_z z)} u(y). \quad (6.17)$$

Insert

$$\left(\frac{\hat{p}_y^2}{2m} + \frac{1}{2m} \left(\hbar k_x + \frac{eB}{c} y \right)^2 + \frac{\hbar k_z^2}{2m} \right) u(y) = E u(y) \quad (6.18)$$

$$\left(\frac{\hat{p}_y^2}{2m} + \frac{1}{2m} \left(\frac{eB}{c} \right)^2 (y_0 + y)^2 + \frac{k_z^2}{2m} \right) u(y) = E u(y) \quad (6.19)$$

with

$$y_0 = \frac{c \hbar k_x}{eB} \quad (6.20)$$

Thus, introducing

$$\begin{aligned} \tilde{k} &= \frac{1}{m} \left(\frac{eB}{c} \right)^2 \\ \tilde{E} &= E - \frac{\hbar k_z^2}{2m} \end{aligned} \quad (6.21)$$

we obtain

$$\left(\frac{\hat{p}_y^2}{2m} + \frac{\tilde{k}}{2} (y + y_0)^2 \right) u(y) = \tilde{E} u(y) \quad (6.22)$$

Thus we can use our results for the one dimensional harmonic oscillator to determine the eigenvalues

$$\tilde{E} = \hbar \omega_L \left(n + \frac{1}{2} \right) \quad (6.23)$$

where

$$\omega_L = \sqrt{\frac{\tilde{k}}{m}} = \frac{eB}{mc} \quad (6.24)$$

is again the Larmor frequency. Thus, we obtain

$$E = \frac{\hbar k_z^2}{2m} + \hbar \omega_L \left(n + \frac{1}{2} \right). \quad (6.25)$$

The eigenfunctions are given by

$$u_n(y) = C_n H_n \left(\sqrt{\frac{m\omega_L}{\hbar}} (y + y_0) \right) \exp \left(-\frac{m\omega_L}{2\hbar} (y + y_0)^2 \right) \quad (6.26)$$

with

$$C_n = \frac{2^{-n/2}}{\sqrt{n!}} \left(\frac{m\omega_L}{\hbar\pi} \right)^{1/4}. \quad (6.27)$$

The total wave function is given by

$$\psi(\mathbf{r}) = e^{i(k_x x + k_y y)} u(y). \quad (6.28)$$

Obviously, the wave function is not symmetric with respect to the components x and y perpendicular to the field. This is not surprising as the phase depends on the specific gauge, and does not need to reflect a physical symmetry. The wave function also demonstrates that in a magnetic field a new length scale

$$l_B = \sqrt{\frac{\hbar}{m\omega_L}} = \sqrt{\frac{\hbar c}{eB}} \quad (6.29)$$

Even though k_x is a continuously varying variable, it does not occur in the energy eigenvalues. Thus, the states we obtained are highly degenerate. To obtain a physical understanding of this issue we realize that y_0 corresponds to the center of the circular orbit of a classical particle in the magnetic field. The corresponding operator

$$\hat{y}_0 = \frac{c\hat{p}_x}{eB} + \hat{y} \quad (6.30)$$

commutes with the Hamiltonian. Similar

$$\hat{x}_0 = \frac{c\hat{p}_y}{eB} + \hat{x} \quad (6.31)$$

commutes with H , but it does not commute with \hat{y}_0 . Thus we have a situation where two operators commute with H but not with each other, implying degenerate states.

To estimate the degeneracy of the Landau levels we consider the motion in a area of size $A = L_x L_y$, such that p_x there are $L_x/(2\pi\hbar)$ values between p_x and $p_x + \Delta p_x$. Using $0 < y_0 < L_y$ yields $\Delta p_x = \frac{eBL_y}{c}$, such that the total degeneracy becomes

$$L_x/(2\pi\hbar) \times \Delta p_x = \frac{eBA}{2\pi\hbar c}. \quad (6.32)$$

This is a macroscopic degeneracy of the Landau levels inside a magnetic field. Essentially the same result can be obtained by packing quasi-classical orbits of area πl_B^2 into the area A yielding $\frac{A}{l_B^2} = \frac{eBA}{\pi\hbar c}$.

6.2.1 Landau levels with spin

We can now combine the results of the previous chapters and obtain for the full Hamiltonian of a non-relativistic particle inside a magnetic field:

$$\hat{H} = \left(\frac{1}{2m} \left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}(\hat{\mathbf{r}}) \right)^2 + e\varphi(\hat{\mathbf{r}}) \right) \sigma^0 + \mu_B \sigma \cdot \mathbf{B}, \quad (6.33)$$

where

$$\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (6.34)$$

The corresponding Schrödinger equation for the spinor state

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \hat{H} \Psi(\mathbf{r}, t) \quad (6.35)$$

is also referred to as the Pauli equation.

Inside a homogeneous field follows

$$\hat{H} = \left(\frac{1}{2m} \left(p_x + \frac{eB}{c} y \right)^2 + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \right) \sigma_0 + \mu_B \boldsymbol{\sigma} \cdot \mathbf{B}. \quad (6.36)$$

Thus we obtain

$$E = \frac{\hbar k_z^2}{2m} + \hbar \omega_L \left(n + m_s + \frac{1}{2} \right). \quad (6.37)$$

6.3 Atom in a magnetic field

We consider a hydrogen atom inside a homogeneous magnetic field. The Hamiltonian is

$$\hat{H} = \left(\frac{1}{2m} \left(\hat{\mathbf{p}} + \frac{e}{c} \mathbf{A}(\hat{\mathbf{r}}) \right)^2 + e\varphi(r) \right) \sigma^0 + \frac{e}{mc} \mathbf{s} \cdot \mathbf{B} \quad (6.38)$$

If we chose

$$\mathbf{A} = \frac{1}{2} (\mathbf{B} \times \mathbf{r}) \quad (6.39)$$

it follows

$$\nabla \cdot \mathbf{A} = 0, \quad (6.40)$$

which implies that $\hat{\mathbf{p}} \mathbf{A}(\hat{\mathbf{r}}) \psi = \mathbf{A}(\hat{\mathbf{r}}) \hat{\mathbf{p}} \psi$, i.e. the momentum operator and the vector potential commute. Thus, it holds

$$\hat{H} = \hat{H}_0 + \frac{e}{mc} \mathbf{A} \cdot \hat{\mathbf{p}} \sigma^0 + \frac{e^2}{2mc^2} \mathbf{A}^2 + \frac{e}{mc} \mathbf{s} \cdot \mathbf{B} \quad (6.41)$$

where \hat{H}_0 is the Hamiltonian without magnetic field. We can insert our choice for the vector potential

$$\begin{aligned} \mathbf{A} \cdot \hat{\mathbf{p}} &= \frac{1}{2} (\mathbf{B} \times \mathbf{r}) \cdot \hat{\mathbf{p}} = \frac{1}{2} \mathbf{B} \cdot (\mathbf{r} \times \hat{\mathbf{p}}) \\ &= \frac{1}{2} \mathbf{B} \cdot \mathbf{L} \end{aligned} \quad (6.42)$$

with angular momentum $\mathbf{L} = \mathbf{r} \times \hat{\mathbf{p}}$. Thus we obtain

$$\hat{H} = \hat{H}_0 + \frac{e}{2mc} (\mathbf{L} + 2\mathbf{s}) \cdot \mathbf{B} + \frac{e^2}{8mc^2} (\mathbf{B} \times \mathbf{r})^2 \quad (6.43)$$

Thus, without field, the presence of the spin leads to an additional degeneracy 2 of each state. Inside a magnetic field, the energy depends explicitly on the angular momentum quantum number m as for $\mathbf{B} = (0, 0, B_z)$ the energy depends on L_z . Finally, the field couples to a total moment

$$\mu_{tot} = -\frac{e}{2mc} (\mathbf{L} + 2\mathbf{s}). \quad (6.44)$$

6.4 Magnetic Monopoles

The Maxwell equations of electrodynamics with electrical charges and currents are

$$\begin{aligned} \nabla \cdot \mathbf{E} &= 4\pi\rho_e \\ \nabla \cdot \mathbf{B} &= 0 \\ -\nabla \times \mathbf{E} &= \frac{\partial \mathbf{B}}{\partial t} \\ \nabla \times \mathbf{B} &= \frac{\partial \mathbf{E}}{\partial t} + 4\pi\mathbf{j}_e \end{aligned} \quad (6.45)$$

Dirac investigated the possibility that there may be magnetic monopoles, i.e. that in fact

$$\begin{aligned} \nabla \cdot \mathbf{E} &= 4\pi\rho_e \\ \nabla \cdot \mathbf{B} &= 4\pi\rho_m \\ -\nabla \times \mathbf{E} &= \frac{\partial \mathbf{B}}{\partial t} + 4\pi\mathbf{j}_m \\ \nabla \times \mathbf{B} &= \frac{\partial \mathbf{E}}{\partial t} + 4\pi\mathbf{j}_e \end{aligned} \quad (6.46)$$

with monopole density ρ_m and magnetic current \mathbf{j}_m .

Let us consider a single such monopole at the origin, i.e.

$$\rho_m = e_m \delta(\mathbf{r}) \quad (6.47)$$

with magnetic charge e_m . The resulting magnetic field is easily obtained from the known electric point charge problem

$$\mathbf{B} = \frac{e_m}{r^2} \mathbf{e}_r \quad (6.48)$$

where \mathbf{e}_r is the unit vector in radial direction. In order to determine the corresponding vector potential we use

$$\begin{aligned} \nabla \times \mathbf{A} &= \mathbf{e}_r \left[\frac{1}{r \sin \theta} \left(\frac{\partial}{\partial \theta} (A_\varphi \sin \theta) - \frac{\partial A_\theta}{\partial \varphi} \right) \right] \\ &+ \mathbf{e}_\theta \frac{1}{r} \left[\frac{1}{\sin \theta} \frac{\partial A_r}{\partial \varphi} - \frac{\partial (r A_\varphi)}{\partial r} \right] + \mathbf{e}_\varphi \frac{1}{r} \left(\frac{\partial (r A_\theta)}{\partial r} - \frac{\partial A_r}{\partial \theta} \right). \end{aligned} \quad (6.49)$$

This suggests

$$\mathbf{A} = \frac{e_m (C - \cos \theta)}{r \sin \theta} \mathbf{e}_\varphi, \quad (6.50)$$

where C is an arbitrary constant. Let us first consider $C = 1$. This vector potential has one difficulty. It is singular on the negative z -axis ($\theta = \pi$). This was to be expected because usually the vector potential is being introduced to guarantee $\nabla \cdot \mathbf{B} = \mathbf{0}$, since $\nabla \cdot \nabla \times \mathbf{A} = \mathbf{0}$ except for regions where \mathbf{A} is singular.

One might now argue that because the vector potential is just a device for obtaining \mathbf{B} , we need not insist on having a single expression for it everywhere. Suppose we construct the potential

$$\begin{aligned} \mathbf{A}^I &= \frac{e_m (1 - \cos \theta)}{r \sin \theta} \mathbf{e}_\varphi \quad \text{if } z > 0 \\ \mathbf{A}^{II} &= \frac{e_m (-1 - \cos \theta)}{r \sin \theta} \mathbf{e}_\varphi \quad \text{if } z < 0, \end{aligned} \quad (6.51)$$

i.e. we chose $C = 1$ for $z > 0$ and $C = -1$ for $z < 0$. Together these potentials lead to the correct expression for \mathbf{B} . Since both potentials lead to the same magnetic field they must be related to each other by a gauge transformation

$$\mathbf{A}^{II} - \mathbf{A}^I = \nabla \chi = -\frac{2e_m}{r \sin \theta} \mathbf{e}_\varphi. \quad (6.52)$$

Lets remember that

$$\nabla \chi = \mathbf{e}_r \frac{\partial \chi}{\partial r} + \mathbf{e}_\theta \frac{1}{r} \frac{\partial \chi}{\partial \theta} + \mathbf{e}_\varphi \frac{1}{r \sin \theta} \frac{\partial \chi}{\partial \varphi} \quad (6.53)$$

we obtain

$$\chi = -2e_m \varphi. \quad (6.54)$$

Changing the gauge implies

$$\psi^{II} = e^{i \frac{e}{\hbar c} \chi} \psi^I, \quad (6.55)$$

which corresponds to

$$\psi^{II}(\theta, \varphi, r) = e^{-i2 \frac{e e_m}{\hbar c} \varphi} \psi^I(\theta, \varphi, r). \quad (6.56)$$

Both wave functions must be single valued. This must be true in particular when we increase the angle φ along the equator and go around once, say from $\varphi = 0$ to $\varphi = 2\pi$:

$$\begin{aligned} \psi^I\left(\theta = \frac{\pi}{2}, \varphi, r\right) &= \psi^I\left(\frac{\pi}{2}, \varphi + 2\pi, r\right) \\ \psi^{II}\left(\theta = \frac{\pi}{2}, \varphi, r\right) &= \psi^{II}\left(\frac{\pi}{2}, \varphi + 2\pi, r\right) \end{aligned} \quad (6.57)$$

Thus, it follows

$$e^{-i2 \frac{e e_m}{\hbar c} 2\pi} \quad (6.58)$$

The uniqueness of the wave function implies therefore:

$$\frac{2ee_m}{\hbar c} = 0, \pm 1, \pm 2 \quad (6.59)$$

Thus, the smallest possible monopole charge is $\frac{\hbar c}{2|e|}$. On the other hand, the existence of magnetic monopoles requires charge quantization.

6.5 The Aharonov-Bohm effect

We consider a double slit experiment supplemented with a solenoid behind the double slit. Inside the solenoid the magnetic field \mathbf{B} is finite, but outside of it, the field vanishes. However, that does not imply that the vector potential vanishes, i.e. for $\nabla \times \mathbf{A} = \mathbf{0}$. In this case the vector potential can always be represented as the gradient of a scalar function. i.e.

$$\mathbf{A}(\mathbf{r}) = \nabla \chi(\mathbf{r}). \quad (6.60)$$

We first study a particle with Hamiltonian

$$\frac{1}{2m} \left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}(\mathbf{r}) \right)^2 \psi(\mathbf{r}) + V(\mathbf{r}) \psi(\mathbf{r}) = E \psi(\mathbf{r}). \quad (6.61)$$

The wave function of a free electron (no spin) within an external magnetic field is given by

$$\psi(\mathbf{r}) = \exp\left(i \frac{e}{\hbar c} \chi(\mathbf{r})\right) \psi_0(\mathbf{r}),$$

where $\psi_0(\mathbf{r})$ is the wave function without the field. This can most directly be seen by inserting this solution:

$$\frac{\hbar}{i} \nabla \psi(\mathbf{r}) = \exp\left(i \frac{e}{\hbar c} \chi(\mathbf{r})\right) \frac{\hbar}{i} \nabla \psi_0(\mathbf{r}) + \psi(\mathbf{r}) \frac{e}{c} \nabla \chi(\mathbf{r}), \quad (6.62)$$

such that for $\nabla \chi(\mathbf{r}) = \mathbf{A}(\mathbf{r})$ follows:

$$\left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}(\mathbf{r}) \right) \psi(\mathbf{r}) = \exp\left(i \frac{e}{\hbar c} \chi(\mathbf{r})\right) \hat{\mathbf{p}} \psi_0(\mathbf{r}). \quad (6.63)$$

Thus yields

$$\begin{aligned} \left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}(\mathbf{r}) \right)^2 \psi(\mathbf{r}) &= \left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}(\mathbf{r}) \right) \exp\left(i \frac{e}{\hbar c} \chi(\mathbf{r})\right) \hat{\mathbf{p}} \psi_0(\mathbf{r}) \\ &= e^{i \frac{e}{\hbar c} \chi(\mathbf{r})} \hat{\mathbf{p}}^2 \psi_0(\mathbf{r}) - \frac{e}{c} \mathbf{A}(\mathbf{r}) e^{i \frac{e}{\hbar c} \chi(\mathbf{r})} \frac{\hbar}{i} \nabla \psi_0(\mathbf{r}) \\ &+ e^{i \frac{e}{\hbar c} \chi(\mathbf{r})} \frac{\hbar}{i} \nabla \psi_0(\mathbf{r}) \frac{e}{c} \nabla \chi(\mathbf{r}), \end{aligned} \quad (6.64)$$

which gives again

$$\left(\hat{\mathbf{p}} - \frac{e}{c} \mathbf{A}(\mathbf{r}) \right)^2 \psi(\mathbf{r}) = e^{i \frac{e}{\hbar c} \chi(\mathbf{r})} \hat{\mathbf{p}}^2 \psi_0(\mathbf{r}). \quad (6.65)$$

It follows

$$\frac{\widehat{\mathbf{p}}^2}{2m}\psi_0(\mathbf{r}) + V(\mathbf{r})\psi_0(\mathbf{r}) = E\psi_0(\mathbf{r}), \quad (6.66)$$

i.e. the wave function corresponds to the case where the vector potential is absent.

In case of $\mathbf{B} = \mathbf{0}$, the energy of the state is unaffected and the wave function magnitude is unaffected. The only difference is therefore the phase change. It holds

$$\chi(\mathbf{r}) = \chi(\mathbf{r}_0) + \int_{\mathbf{r}_0}^{\mathbf{r}} \mathbf{A}(\mathbf{r}') \cdot d\mathbf{r}'. \quad (6.67)$$

One has to be careful with this integration. It cannot wind around the solenoid. The reason is that the function χ is either not unique or not differentiable. This becomes evident if we analyze the vector potential of a solenoid

$$\mathbf{A}(\mathbf{r}) = \frac{\Phi}{2\pi r} \mathbf{e}_\varphi \quad (6.68)$$

which leads to $\chi = \frac{\Phi}{2\pi}\varphi$, where φ is the polar angle relative to the center of the solenoid. performing the integration in such a way that the curve contains a loop around the solenoid yields that $\chi \rightarrow \chi + \Phi$. However, for our problem we need a locally unique function $\chi(\mathbf{r})$, which can be obtained if one avoids the mentioned loops around the solenoid. If the solenoid is located behind the double slit and if the design it such that the particle never enters the region with finite \mathbf{B} field, there is nevertheless a measurable effect.

If we now write the wave function originating in the two slits as

$$\begin{aligned} \psi^{(1)}(\mathbf{r}) &= \psi_0^{(1)}(\mathbf{r}) e^{i\frac{e}{\hbar c}\chi^{(1)}(\mathbf{r})} \\ \psi^{(2)}(\mathbf{r}) &= \psi_0^{(2)}(\mathbf{r}) e^{i\frac{e}{\hbar c}\chi^{(2)}(\mathbf{r})} \end{aligned} \quad (6.69)$$

and the total wave function as

$$\psi(\mathbf{r}) = \psi^{(1)}(\mathbf{r}) + \psi^{(2)}(\mathbf{r}) \quad (6.70)$$

which is then characterized by an interference term determined by the phase difference

$$\Delta\phi = \chi^{(1)}(\mathbf{r}) - \chi^{(2)}(\mathbf{r}). \quad (6.71)$$

The phase difference between two paths that avoid the solenoid is then

$$\Delta\phi = \frac{e}{\hbar c} \oint \mathbf{A}(\mathbf{r}) \cdot d\mathbf{r} = \frac{e}{\hbar c} \int_A \mathbf{B} \cdot d\mathbf{f}. \quad (6.72)$$

Thus there is a measurable phase difference between the two paths that is expressed in terms of the flux

$$\Phi = \int_A \mathbf{B} \cdot d\mathbf{f} \quad (6.73)$$

of the solenoid. This phenomenon is called the Aharonov Bohm effect. The key aspect of this result is that a quantum particle, given the non-locality of the wave function, “feels” the magnetic field even though it never penetrates the regime of a finite \mathbf{B} -field.

Chapter 7

Pictures in quantum mechanics

The time dependent Schrödinger equation

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \hat{H} \psi(\mathbf{r}, t) \quad (7.1)$$

determines the time dependence of the wave function. In case of a time independent Hamiltonian it is even possible to determine a formal solution of the type:

$$\psi(\mathbf{r}, t) = e^{-\frac{it\hat{H}}{\hbar}} \psi(\mathbf{r}, 0). \quad (7.2)$$

Whenever we are considering a function $f(\hat{O})$ of an operator, it is really only defined via the Taylor expansion of that function. Let

$$f(x) = \sum_m f_m x^m \quad (7.3)$$

be the Taylor expansion of f , we have

$$f(\hat{O}) = \sum_{m=0}^{\infty} f_m \hat{O}^m. \quad (7.4)$$

Arbitrary powers of an operator are of course well defined. If $|n\rangle$ are the eigenfunctions of \hat{O} with eigenvalue o_n it holds

$$f(\hat{O}) |n\rangle = \sum_{m=0}^{\infty} f_m \hat{O}^m |n\rangle. \quad (7.5)$$

Using $\hat{O}^m |n\rangle = o_n^m |n\rangle$ we obtain

$$f(\hat{O}) |n\rangle = \sum_{m=0}^{\infty} f_m o_n^m |n\rangle = f(o_n) |n\rangle. \quad (7.6)$$

Thus, $f(o_n)$ is the eigenvalue of the operator $f(\hat{O})$, if o_n is the eigenvalue of \hat{O} .

Using these results we can now show that the above formal solution solves the Schrödinger equation. This can be explicitly shown by expanding

$$\psi(\mathbf{r}, 0) = \sum_n a_n \varphi_n(\mathbf{r}, 0). \quad (7.7)$$

into the set of eigenfunctions of the Hamiltonian. Using

$$e^{-\frac{i t \hat{H}}{\hbar}} \varphi_n(\mathbf{r}, 0) = e^{-i \frac{E_n t}{\hbar}} \varphi_n(\mathbf{r}, 0) \quad (7.8)$$

gives the result we obtained earlier

$$\psi(\mathbf{r}, t) = \sum_n a_n e^{-i \frac{E_n t}{\hbar}} \varphi_n(\mathbf{r}, 0). \quad (7.9)$$

We can now insert this function into the Schrödinger equation and find that $i\hbar \frac{\partial}{\partial t}$ has the same effect as applying the Hamiltonian, i.e. it solves the Schrödinger equation.

This result suggests to introduce the operator

$$\hat{U}(t, t') = e^{-\frac{i(t-t')\hat{H}}{\hbar}} \quad (7.10)$$

that determines the time-evolution of the wave function. The inverse of the time evolution operator, defined via

$$\hat{U}(t, t')^{-1} \hat{U}(t, t') = 1 \quad (7.11)$$

is given as

$$\hat{U}(t, t')^{-1} = e^{\frac{i(t-t')\hat{H}}{\hbar}}. \quad (7.12)$$

It corresponds to the backwards evolution of the state. To check that this is the case we consider the general case of an operator

$$e^{i\hat{S}} = 1 + i\hat{S} - \frac{1}{2}\hat{S}^2 \dots, \quad (7.13)$$

we can then show that

$$e^{-i\hat{S}} = 1 - i\hat{S} - \frac{1}{2}\hat{S}^2 \dots \quad (7.14)$$

is indeed the inverse operator. Multiplying both operators yields

$$\begin{aligned} e^{i\hat{S}} e^{-i\hat{S}} &= \left(1 + i\hat{S} - \frac{1}{2}\hat{S}^2\right) \left(1 - i\hat{S} - \frac{1}{2}\hat{S}^2\right) \\ &= 1 + i\hat{S} - i\hat{S} - \hat{S}^2 + \hat{S}^2 \dots \\ &= 1. \end{aligned} \quad (7.15)$$

This demonstrates in particular that \hat{U}^{-1} is the inverse of \hat{U} . Another interesting property of the time-evolution operator follows from the fact that it has the form $e^{i\hat{S}}$, where \hat{S} is an Hermitian operator. It follows for the adjoint or hermitian conjugate operator that

$$\begin{aligned} \left(e^{i\hat{S}}\right)^\dagger &= \left(1 + i\hat{S} - \frac{1}{2}\hat{S}^2 \dots\right)^\dagger \\ &= 1 - i\hat{S}^\dagger - \frac{1}{2}\left(\hat{S}^2\right)^\dagger \dots \end{aligned} \quad (7.16)$$

Since S is Hermitian it holds

$$\left(\hat{S}^m\right)^\dagger = \hat{S}^\dagger \dots \hat{S}^\dagger = \hat{S} \dots \hat{S} = \hat{S}^m \quad (7.17)$$

and we obtain

$$\left(e^{i\hat{S}}\right)^\dagger = e^{-i\hat{S}}. \quad (7.18)$$

Thus we found that $\hat{U}^{-1} = \hat{U}^\dagger$, which defines a unitary transformation. Let us consider two states

$$\begin{aligned} |\varphi\rangle &= \hat{U} |\varphi'\rangle \\ |\psi\rangle &= \hat{U} |\psi'\rangle \end{aligned} \quad (7.19)$$

where U is a unitary transformation. It follows immediately

$$\begin{aligned} \langle\varphi|\psi\rangle &= \langle\varphi'|\hat{U}^\dagger\hat{U}|\psi'\rangle \\ &= \langle\varphi'|\hat{U}^{-1}\hat{U}|\psi'\rangle = \langle\varphi'|\psi'\rangle. \end{aligned} \quad (7.20)$$

We find that a unitary transformation has the interesting property that it conserves scalar products, including the norm of states. Thus, the time evolution dictated by quantum mechanics is unitary.

Let us now consider an operator equation of the type

$$\hat{O}|\varphi(t)\rangle = |\psi(t)\rangle, \quad (7.21)$$

with some operator and with wave functions that are time dependent. We can now express those states as time evolved from some arbitrary initial time, say $t' = 0$:

$$\begin{aligned} |\varphi(t)\rangle &= \hat{U}(t,0)|\varphi_0\rangle \\ |\psi(t)\rangle &= \hat{U}(t,0)|\psi_0\rangle \end{aligned} \quad (7.22)$$

It follows

$$\hat{O}\hat{U}(t,0)|\varphi_0\rangle = \hat{U}(t,0)|\psi_0\rangle \quad (7.23)$$

We multiply this equation with $\hat{U}^\dagger(t,0)$ from the left and obtain

$$\hat{O}(t)|\varphi_0\rangle = |\psi_0\rangle, \quad (7.24)$$

where

$$\hat{O}(t) = \hat{U}(t, 0)^{-1} \hat{O} \hat{U}(t, 0). \quad (7.25)$$

Thus, we can transform an equation where the operators are time independent and the wave functions are time dependent into an equivalent form where the operators are time-dependent and the wave functions are not. Any matrix element and observable, can be determined either in one or in the other form. Since scalar products do not change under a unitary transformation, it doesn't matter which approach one uses.

Thus we introduce the transformation of the wave functions from the Schrödinger to the Heisenberg picture.

$$|\varphi_H\rangle = e^{\frac{i t \hat{H}}{\hbar}} |\varphi(t)\rangle \quad (7.26)$$

along with corresponding transformation of the operators:

$$O_H(t) = e^{\frac{i t \hat{H}}{\hbar}} O(t) e^{-\frac{i t \hat{H}}{\hbar}}, \quad (7.27)$$

where we even allowed for some explicit time dependence of the operator. It follows

$$\frac{dO_H(t)}{dt} = \frac{de^{\frac{i t \hat{H}}{\hbar}}}{dt} O(t) e^{-\frac{i t \hat{H}}{\hbar}} + e^{\frac{i t \hat{H}}{\hbar}} O(t) \frac{de^{-\frac{i t \hat{H}}{\hbar}}}{dt} + e^{\frac{i t \hat{H}}{\hbar}} \frac{\partial O(t)}{\partial t} e^{-\frac{i t \hat{H}}{\hbar}}. \quad (7.28)$$

In order to perform the derivatives we use that:

$$e^{-\frac{i(t+\varepsilon)\hat{H}}{\hbar}} = e^{-\frac{i t \hat{H}}{\hbar}} \left(1 - \frac{i\varepsilon}{\hbar} \hat{H}\right), \quad (7.29)$$

which gives

$$i\hbar \frac{de^{-\frac{i t \hat{H}}{\hbar}}}{dt} = e^{-\frac{i t \hat{H}}{\hbar}} \hat{H}. \quad (7.30)$$

Thus, it follows the Heisenberg equation of motion:

$$i\hbar \frac{dO_H(t)}{dt} = [O_H(t), H] + i\hbar \frac{\partial O_H(t)}{\partial t} \quad (7.31)$$

Since the wave function is time independent, we do not need to bother looking at its time evolution. The time evolution is instead one of the operators that are governed by the above equation of motion.

Example: precession of a spin in a magnetic field. We chose $\mathbf{B} = (0, 0, B)$ and obtain:

$$\begin{aligned} \hat{H} &= -\gamma \mathbf{s} \cdot \mathbf{B} = \mu_B \sigma \cdot \mathbf{B} \\ &= \mu_B B \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned} \quad (7.32)$$

It obviously holds $[s_z, H]$ and we obtain for the spin operator in Heisenberg picture:

$$\frac{ds_z(t)}{dt} = 0. \quad (7.33)$$

Next we analyze $s_x(t)$. Since there is no explicit time dependence it follows

$$i\hbar \frac{ds_x(t)}{dt} = [s_x, \hat{H}] = -\gamma B [s_x, s_z] = i\hbar\gamma B s_y \quad (7.34)$$

and similarly

$$i\hbar \frac{ds_y(t)}{dt} = [s_y, \hat{H}] = -\gamma B [s_y, s_z] = -i\hbar\gamma B s_x \quad (7.35)$$

which gives

$$\frac{d^2 s_x(t)}{dt^2} = -\gamma^2 B^2 s_x \quad (7.36)$$

which is solved via

$$\begin{aligned} s_x(t) &= ae^{i\omega_L t} + be^{-i\omega_L t} \\ s_y(t) &= i(ae^{i\omega_L t} - be^{-i\omega_L t}) \end{aligned} \quad (7.37)$$

with

$$\omega_L = \gamma B = \frac{eB}{mc}. \quad (7.38)$$

Thus

$$\begin{aligned} a + b &= s_x(0) \\ i(a - b) &= s_y(0) \end{aligned} \quad (7.39)$$

yielding

$$\begin{aligned} a &= \frac{1}{2}(s_x(0) - is_y(0)) \\ b &= \frac{1}{2}(s_x(0) + is_y(0)) \end{aligned} \quad (7.40)$$

In addition to the so called Schrödinger and Heisenberg pictures, there is also an intermediate possibility that plays an important role in the time dependent perturbation theory (that will not be part of this lecture). For completeness, we still mention the basic idea of this interaction picture. Let us consider a Hamiltonian of the form

$$H = H_0 + V(t) \quad (7.41)$$

We now strip off the time dependence that is caused by the (usually simpler) Hamiltonian H_0

$$|\varphi_I(t)\rangle = e^{\frac{it\hat{H}_0}{\hbar}} |\varphi(t)\rangle \quad (7.42)$$

and transfer it to the time dependence of the operators:

$$O_I(t) = e^{\frac{it\hat{H}_0}{\hbar}} O(t) e^{-\frac{it\hat{H}_0}{\hbar}}. \quad (7.43)$$

We can now determine the equation of motion for the wave function in the interaction representation, which follows as

$$i\hbar \frac{\partial |\varphi_I(t)\rangle}{\partial t} = V |\varphi_I(t)\rangle. \quad (7.44)$$

with formal solution:

$$|\varphi_I(t)\rangle = |\varphi_I(t_0)\rangle + \frac{1}{i\hbar} \int_{t_0}^t V(t') |\varphi_I(t')\rangle dt'. \quad (7.45)$$

The real appeal of this split approach will only become clear in the context of time dependent perturbation theory. It also plays a fundamental role in the perturbative formulation of quantum field theory.

Chapter 8

Particle in a central potential

We consider a system of two particles with a potential $V(\mathbf{r}_1 - \mathbf{r}_2)$ that only depends on the distance between these particles

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\mathbf{r}_1 - \mathbf{r}_2). \quad (8.1)$$

We introduce center of gravity and relative coordinates

$$\begin{aligned} \mathbf{R} &= \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \\ \mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2 \end{aligned} \quad (8.2)$$

yielding

$$H = -\frac{\hbar^2}{2(m_1 + m_2)}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}). \quad (8.3)$$

with reduced mass m determined by

$$\frac{1}{m} = \frac{1}{m_1} + \frac{1}{m_2}. \quad (8.4)$$

The center of gravity behaves just like a free particle while the relative coordinate behaves like a particle in a potential. In what follows we assume that the potential only depends on the magnitude $r = |\mathbf{r}|$ of the vector \mathbf{r} and not on its direction:

$$V(\mathbf{r}) = V(r). \quad (8.5)$$

This is what is called a central potential.

The Schrödinger equation of the relative motion is then given as

$$\left(-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V(r)\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}). \quad (8.6)$$

Using our previous results for the Laplacian in spherical coordinates we write

$$\left(\frac{1}{2m} \left[\widehat{p}_r^2 + \frac{\widehat{\mathbf{L}}^2}{r^2} \right] + V(r) \right) \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (8.7)$$

with

$$\widehat{p}_r = -i\hbar \frac{1}{r} \frac{\partial}{\partial r} r \quad (8.8)$$

We make the product ansatz

$$\psi(\mathbf{r}) = R(r) y(\theta, \varphi) \quad (8.9)$$

and obtain

$$\left(\frac{1}{2m} \widehat{p}_r^2 + \frac{1}{2m} \frac{\widehat{\mathbf{L}}^2}{r^2} + V(r) \right) R(r) y(\theta, \varphi) = ER(r) y(\theta, \varphi) \quad (8.10)$$

gives

$$\frac{r^2}{R(r)} \widehat{p}_r^2 R(r) + (V(r) - E) 2mr^2 = \frac{1}{y(\theta, \varphi)} \widehat{\mathbf{L}}^2 y(\theta, \varphi) = C \quad (8.11)$$

Thus we have to solve

$$\widehat{\mathbf{L}}^2 y(\theta, \varphi) = Cy(\theta, \varphi) \quad (8.12)$$

and we obtain immediately

$$y(\theta, \varphi) = Y_{lm}(\theta, \varphi) \quad (8.13)$$

and $C = \hbar^2 l(l+1)$. It then follows

$$\left(\frac{1}{2m} \widehat{p}_r^2 + V_{eff}(r) \right) R(r) = ER(r) \quad (8.14)$$

with

$$V_{eff}(r) = V(r) + \frac{1}{2m} \frac{\hbar^2 l(l+1)}{r^2}. \quad (8.15)$$

8.1 The hydrogen atom

The potential is

$$V(r) = -\frac{e^2}{r}. \quad (8.16)$$

The wave function is again assumed to be

$$\psi(\mathbf{r}) = R(r) Y_{lm}(\theta, \varphi) \quad (8.17)$$

and the only part that determines on the potential is the radial wave function

$$\left(\frac{1}{2m} \widehat{p}_r^2 + V_{eff}(r) \right) R(r) = ER(r) \quad (8.18)$$

with

$$V_{eff}(r) = -\frac{e^2}{r} + \frac{1}{2m} \frac{\hbar^2 l(l+1)}{r^2}. \quad (8.19)$$

Introducing

$$u(r) = rR(r) \quad (8.20)$$

we obtain

$$\left(-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \frac{2m e^2}{\hbar^2 r} - \frac{2mE}{\hbar^2} \right) u(r) = 0 \quad (8.21)$$

Next, we make the substitution

$$\begin{aligned} x &= 2\kappa r \\ \frac{\hbar^2 \kappa^2}{2m} &= -E \\ n^2 &= -\frac{R_0}{E} \end{aligned} \quad (8.22)$$

where

$$x = \frac{2Z}{n} \frac{r}{a_0} \quad (8.23)$$

$$R_0 = \frac{\hbar^2}{2ma_0^2} \quad (8.24)$$

is the Rydberg constant and

$$a_0 = \frac{\hbar^2}{me^2} \quad (8.25)$$

is the Bohr radius. They are given by

$$\begin{aligned} R_0 &= 13.6056981 \text{eV} = 2.1798741 \times 10^{-18} \text{J} \\ a_0 &= 0.529177249 \times 10^{-10} \text{m}. \end{aligned} \quad (8.26)$$

In these variables it holds

$$\frac{d^2 u}{dx^2} - \frac{l(l+1)}{x^2} u + \left(\frac{n}{x} - \frac{1}{4} \right) u = 0. \quad (8.27)$$

For large values of x the equation reduces to

$$\frac{d^2 u}{dx^2} - \frac{u}{4} = 0 \quad (8.28)$$

so that

$$u \propto e^{\pm x/2} \quad (8.29)$$

where we discard the positive sign as it is inconsistent with a bound state. For small x it follows

$$\frac{d^2 u}{dx^2} - \frac{l(l+1)}{x^2} u = 0. \quad (8.30)$$

Substitution of the ansatz $u = \rho^q$ gives

$$q(q-1) = l(l+1) \quad (8.31)$$

which yields

$$u = Ax^{-l} + Bx^{l+1} \quad (8.32)$$

In order for u to vanish at the origin we chose $A = 0$.

To cover the entire x regime we make the ansatz

$$u(x) = x^{l+1} e^{-x/2} F(x) \quad (8.33)$$

where $F(\rho)$ is finite everywhere. Thus we assume

$$F(x) = \sum_{n=0}^{\infty} C_n x^n. \quad (8.34)$$

Substituting the above ansatz for u into the differential equation gives

$$\left[x \frac{d^2}{dx^2} + (2l+2-\rho) \frac{d}{dx} - (l+1-n) \right] F(x) = 0 \quad (8.35)$$

Inserting the power-law ansatz gives

$$C_{i+1} = \frac{(i+l+1)-n}{(i+1)(i+2l+2)} C_i \equiv \Gamma_{i,l} C_i \quad (8.36)$$

If the recursion relation continues to large i it holds

$$C_{i+1} \simeq \frac{1}{i} C_i \quad (8.37)$$

which corresponds to $F(\rho) \propto e^\rho$. This leads to a divergent wave function and requires that $\Gamma_{i,l} = 0$ above some i . Thus at the maximal value for i it holds

$$(i_{\max} + l + 1) - n = 0 \quad (8.38)$$

Thus n must be an integer. It then follows

$$E_n = -\frac{1}{n^2} R_0. \quad (8.39)$$

It is obvious that $n \geq 1$ as $n = 0$ will not lead to a termination of the recursion. It obviously holds that $i_{\max} \geq 0$ which gives

$$n \geq l + 1. \quad (8.40)$$

We notice that the energy eigenvalues do not depend on the angular momentum quantum number l , an effect typically referred to as accidental degeneracy. For

given l we have a degeneracy $2l + 1$, reflecting the different values m can take. Because of $n \geq l + 1$ holds that the total degeneracy is

$$g_n = \sum_{l=0}^{n-1} (2l + 1) = (n - 1)n + n = n^2. \quad (8.41)$$

The polynomials $F_{n,l}(x)$ are of order $n - l - 1$ and are known as associated Laguerre polynomials $L_{n-l-1}^{2l+1}(x)$ that can be determined as

$$L_p^q(x) = (-1)^q \frac{d^q}{dx^q} L_{p+q}(x) \quad (8.42)$$

where

$$L_p(x) = e^x \frac{d^p}{dx^p} x^p e^{-x}. \quad (8.43)$$

It holds for example:

$$\begin{aligned} L_1(x) &= 1 - x \\ L_2(x) &= 1 - 2x + \frac{x^2}{2}. \end{aligned} \quad (8.44)$$

The characteristic length scale of the wave function is determined by our dimensionless units:

$$\begin{aligned} r &= \lambda x \\ \frac{1}{4} \frac{\hbar^2}{2m\lambda^2} &= -E_n \end{aligned} \quad (8.45)$$

Thus

$$\lambda_n = \frac{na_0}{2} \quad (8.46)$$

The characteristic length scale is therefore dependent on the principle quantum number. The larger n the further away from the nucleus is the electron located.

The usual notation is to refer to the different l values as

$$\begin{array}{cccccc} l & 0 & 1 & 2 & 3 & 4 \\ \text{code} & s & p & d & f & g \end{array} \quad (8.47)$$

such that a state with $n = 1$ and $l = 0$ is called $1s$, a state with $n = 2$ and $l = 0$ as $2s$ a state with $n = 2$ and $l = 1$ as $2p$, a state with $n = 3$, $l = 2$ as $3d$ or a state with $n = 4$ and $l = 3$ as $4f$ etc.

The corresponding wave functions $\psi_{n,l,m}(\mathbf{r})$ can then be explicitly given as

$$\begin{aligned}
\psi_{1,0,0}(\mathbf{r}) &= \frac{2}{a_0^{3/2}} e^{-r/a_0} Y_{0,0}(\theta, \varphi) \\
\psi_{2,0,0}(\mathbf{r}) &= \frac{2}{(2a_0)^{3/2}} \left(1 - \frac{r}{2a_0}\right) e^{-r/(2a_0)} Y_{0,0}(\theta, \varphi) \\
\begin{pmatrix} \psi_{2,1,1}(\mathbf{r}) \\ \psi_{2,1,0}(\mathbf{r}) \\ \psi_{2,1,-1}(\mathbf{r}) \end{pmatrix} &= \frac{1}{\sqrt{3} (2a_0)^{3/2} a_0} e^{-r/(2a_0)} \begin{pmatrix} Y_{1,1}(\theta, \varphi) \\ Y_{1,0}(\theta, \varphi) \\ Y_{1,-1}(\theta, \varphi) \end{pmatrix} \\
\psi_{3,0,0}(\mathbf{r}) &= \frac{2}{3 (3a_0)^{3/2}} \left(3 - \frac{2r}{a_0} + \frac{2r^2}{9a_0^2}\right) e^{-r/(3a_0)} Y_{0,0}(\theta, \varphi) \\
\begin{pmatrix} \psi_{3,1,1}(\mathbf{r}) \\ \psi_{3,1,0}(\mathbf{r}) \\ \psi_{3,1,-1}(\mathbf{r}) \end{pmatrix} &= \frac{4\sqrt{2}}{9 (3a_0)^{3/2} a_0} e^{-r/(3a_0)} \begin{pmatrix} Y_{1,1}(\theta, \varphi) \\ Y_{1,0}(\theta, \varphi) \\ Y_{1,-1}(\theta, \varphi) \end{pmatrix} \\
\begin{pmatrix} \psi_{3,2,2}(\mathbf{r}) \\ \psi_{3,2,1}(\mathbf{r}) \\ \psi_{3,2,0}(\mathbf{r}) \\ \psi_{3,2,-1}(\mathbf{r}) \\ \psi_{3,2,-2}(\mathbf{r}) \end{pmatrix} &= \frac{2\sqrt{2}}{27\sqrt{5} (3a_0)^{3/2} a_0^2} e^{-r/(3a_0)} \begin{pmatrix} Y_{2,2}(\theta, \varphi) \\ Y_{2,1}(\theta, \varphi) \\ Y_{2,0}(\theta, \varphi) \\ Y_{2,-1}(\theta, \varphi) \\ Y_{2,-2}(\theta, \varphi) \end{pmatrix}.
\end{aligned}$$

Chapter 9

Time independent Perturbation theory

An exact solution of a quantum mechanical problem exists only in rather few cases. In many situations it is therefore important to use approximate methods to gain qualitative insight into the properties of a physical system. Progress can be made if the Hamiltonian can be split into two contributions:

$$H = H_0 + V. \quad (9.1)$$

Here H_0 is the *unperturbed* part of the Hamiltonian. We assume that we know the solution of the Schrödinger equation

$$H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}. \quad (9.2)$$

The second part of the Hamiltonian is the *perturbation* V which we assume to be small. What exactly we mean by smallness will be specified as we go along. In what follows we consider three cases: time independent non-degenerate perturbation theory, time independent degenerate perturbation theory and time dependent perturbation theory.

In case of time independent perturbation theory we assume that V does not depend explicitly on time. Thus, we need to solve the Schrödinger equation

$$H\psi_n = E_n\psi_n. \quad (9.3)$$

For the formal analysis of the theory it is useful to introduce a dimensionless variable λ such that

$$H_\lambda = H_0 + \lambda V \quad (9.4)$$

and expand the wave functions and eigenvalues as a power series in λ

$$\begin{aligned} \psi_n &= \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \dots \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{aligned} \quad (9.5)$$

Inserting this ansatz into the Schrödinger equation and sorting terms according to their order in λ yields the following set of equations: At zeroth order in λ follows as expected

$$H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}. \quad (9.6)$$

At first order in λ follows

$$H_0\psi_n^{(1)} + V\psi_n^{(0)} = E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)} \quad (9.7)$$

while at second order holds

$$H_0\psi_n^{(2)} + V\psi_n^{(1)} = E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(0)}\psi_n^{(2)}. \quad (9.8)$$

Before we solve Eq.9.7 we note that there is a certain ambiguity: if $\psi_n^{(1)}$ is a solution, so is $\psi_n^{(1)} + a\psi_n^{(0)}$. This follows by inserting this solution into Eq.9.7. Since we want to preserve normalization of the wave function it follows up to first order in λ :

$$1 = \langle \psi_n | \psi_n \rangle \simeq \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \lambda \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \lambda \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle \quad (9.9)$$

We require $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$ since $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1$. This fixes the above ambiguity.

9.1 Non-degenerate perturbation theory

We first consider the situation of non-degenerate time independent perturbation theory. We assume that the unperturbed eigenvalues $E_n^{(0)}$ are all distinct. We first consider the first order correction of Eq.9.7. We expand the wave function $\psi_n^{(1)}$ w.r.t. the unperturbed wave functions $\psi_l^{(0)}$:

$$\psi_n^{(1)} = \sum_l c_{nl}\psi_l^{(0)}. \quad (9.10)$$

Since $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = 0$ it follows immediately that $c_{nn} = 0$. Inserting this result into Eq.9.7 gives

$$\sum_l c_{nl}H_0\psi_l^{(0)} + V\psi_n^{(0)} = E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\sum_l c_{nl}\psi_l^{(0)}. \quad (9.11)$$

We multiply this equation from the left with $\psi_m^{(0)}$ and integrate over space. It follows

$$c_{nm}E_m^{(0)} + \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle = E_n^{(1)}\delta_{nm} + E_n^{(0)}c_{nm}. \quad (9.12)$$

In case of $n = m$ follows

$$E_n^{(1)} = V_{nn} \equiv \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle, \quad (9.13)$$

while for $n \neq m$ holds that

$$c_{nm} = \frac{\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}. \quad (9.14)$$

Thus we obtain for the wave function to first order

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)} \quad (9.15)$$

In order to analyze the second order corrections we analyze Eq.9.8. We expand again in terms of the non-perturbed wave functions

$$\psi_n^{(2)} = \sum_l d_{nl} \psi_l^{(0)} \quad (9.16)$$

and insert this into Eq.9.8.

$$\sum_l E_l^{(0)} d_{nl} \psi_l^{(0)} + V \psi_n^{(1)} = E_n^{(2)} \psi_n^{(0)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(0)} \sum_l d_{nl} \psi_l^{(0)} \quad (9.17)$$

We multiply this equation again from the left with $\psi_m^{(0)}$ and integrate over space. It follows

$$E_m^{(0)} d_{nm} + \langle \psi_m^{(0)} | V | \psi_n^{(1)} \rangle = E_n^{(2)} \delta_{nm} + E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle + E_n^{(0)} d_{nm} \quad (9.18)$$

We consider $n = m$ and obtain

$$\begin{aligned} E_n^{(2)} &= \langle \psi_n^{(0)} | V | \psi_n^{(1)} \rangle \\ &= \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | V | \psi_m^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} \\ &= \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \end{aligned} \quad (9.19)$$

We observe the interesting effect that the second order correction to the ground state is negative $E_{n=0}^{(2)} \leq 0$.

If we consider $n \neq m$ we obtain

$$d_{nm} = \frac{E_n^{(1)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle - \langle \psi_m^{(0)} | V | \psi_n^{(1)} \rangle}{E_m^{(0)} - E_n^{(0)}}. \quad (9.20)$$

The coefficient d_{mn} can be obtained by ensuring normalization of the wave function.

We summarize the result for the energy eigenvalues in perturbation theory:

$$E_n = E_n^{(0)} + V_{nn} + \sum_{m \neq n} \frac{|V_{mn}|^2}{E_n^{(0)} - E_m^{(0)}} + \dots \quad (9.21)$$

with $V_{mn} = \langle \psi_m^{(0)} | V | \psi_n^{(0)} \rangle$.

9.1.1 Example: anharmonic oscillator

We consider the anharmonic oscillator with unperturbed part of the Hamiltonian:

$$H_0 = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 \hat{x}^2}{2} \quad (9.22)$$

and perturbation

$$V = \gamma \hat{x}^3. \quad (9.23)$$

Before we start we note that this problem is ill defined if we tried to determine the exact solution of the Hamiltonian $H_0 + V$. Depending on the sign of γ , a particle would always disappear to $x \rightarrow \pm\infty$ where the potential approaches $V \rightarrow -\infty$. Within perturbation theory we do not recognize this effect as the solution will always be close to the unperturbed one.

It is useful to determine the appropriate dimensionless coupling constant of the problem. From the solution of the harmonic oscillator we know that the characteristic length scale of the problem is $x_0 = \sqrt{\frac{\hbar}{m\omega}}$, while the characteristic energy scale is $\hbar\omega$. Thus we write

$$V = \frac{\gamma x_0^3}{\hbar\omega} \left(\frac{\hat{x}}{x_0} \right)^3 \hbar\omega = \Gamma \left(\frac{\hat{x}}{x_0} \right)^3 \hbar\omega \quad (9.24)$$

where

$$\Gamma = \frac{\gamma x_0^3}{\hbar\omega} = \frac{\gamma}{\hbar\omega} \left(\frac{\hbar}{m\omega} \right)^{3/2} \quad (9.25)$$

is the the appropriate dimensionless strength of the potential V . Therefore, we suspect that $\Gamma \ll 1$ is the appropriate small parameter of the theory.

The first order correction to the energy vanishes

$$E_n^{(1)} = \gamma \int dx \psi(x)^* x^3 \psi(x) = 0 \quad (9.26)$$

since $|\psi(x)|^2$ is an even function and x^3 is odd. Thus we analyze the second order correction. In order to proceed we need to determine the matrix element:

$$\langle m | \hat{x}^3 | n \rangle = \sum_{l,r} \langle m | \hat{x} | l \rangle \langle l | \hat{x} | r \rangle \langle r | \hat{x} | n \rangle \quad (9.27)$$

We substitute our earlier result for the matrix element of the position operator of the harmonic oscillator

$$\langle m | \hat{x} | n \rangle = \sqrt{\frac{\hbar}{2m\omega}} (\sqrt{n+1}\delta_{m,n+1} + \sqrt{n}\delta_{m,n-1}) \quad (9.28)$$

$$\begin{aligned} \langle m | \hat{x}^2 | n \rangle &= \frac{\hbar}{2m\omega} \sum_l (\sqrt{l+1}\delta_{m,l+1} + \sqrt{l}\delta_{m,l-1}) (\sqrt{n+1}\delta_{l,n+1} + \sqrt{n}\delta_{l,n-1}) \\ &= \frac{\hbar}{2m\omega} (\sqrt{(n+2)(n+1)}\delta_{m,n+2} + (2n+1)\delta_{m,n} + \sqrt{(n-1)n}\delta_{m,n-2}). \end{aligned}$$

This yields

$$\begin{aligned} \frac{\langle m | \hat{x}^3 | n \rangle}{\left(\frac{\hbar}{2m\omega}\right)^{3/2}} &= \sqrt{(n+1)(n+2)(n+3)}\delta_{m,n+3} \\ &\quad + \sqrt{n(n-1)(n-3)}\delta_{m,n-3} \\ &\quad + 3(n+1)^{3/2}\delta_{m,n+1} + 3n^{3/2}\delta_{m,n-1}. \end{aligned} \quad (9.29)$$

For the ground state $n = 0$, there are two nonzero matrix elements:

$$\begin{aligned} \langle 1 | V | 0 \rangle &= 3\gamma \left(\frac{\hbar}{2m\omega}\right)^{3/2} \\ \langle 3 | V | 0 \rangle &= \sqrt{6}\gamma \left(\frac{\hbar}{2m\omega}\right)^{3/2} \end{aligned} \quad (9.30)$$

Thus we obtain

$$\begin{aligned} E_0^{(2)} &= \frac{|\langle 1 | V | 0 \rangle|^2}{E_0^{(0)} - E_1^{(0)}} + \frac{|\langle 3 | V | 0 \rangle|^2}{E_0^{(0)} - E_3^{(0)}} \\ &= -\frac{9\gamma^2 \left(\frac{\hbar}{2m\omega}\right)^3}{\hbar\omega} - \frac{6\gamma^2 \left(\frac{\hbar}{2m\omega}\right)^3}{3\hbar\omega} \\ &= -\frac{11\gamma^2 \left(\frac{\hbar}{m\omega}\right)^3}{8\hbar\omega} = -\frac{11}{8}\Gamma^2\hbar\omega \end{aligned} \quad (9.31)$$

and we find

$$E_0 = \frac{1}{2}\hbar\omega - \frac{11\gamma^2\hbar^2}{8m^3\omega^4} = \frac{\hbar\omega}{2} \left(1 - \frac{11}{4}\Gamma^2\right) \quad (9.32)$$

As expected, the second order correction is small for $\Gamma \ll 1$.

9.2 Degenerate perturbation theory

Next we analyze the problem of degeneracy for the unperturbed problem. Thus, we consider the situation where the states $\psi_n^{(0)}, \dots, \psi_{n+q}^{(0)}$ all have the same

energy: $E_n^{(0)} = E_{n+1}^{(0)} = \dots = E_{n+q}^{(0)}$. To proceed we keep in mind that any linear combination

$$\tilde{\psi}_l^{(0)} = \sum_{m=n}^{n+q} \alpha_{lm} \psi_m^{(0)} \quad (9.33)$$

is also an eigenfunction with same eigenvalue $E_n^{(0)}$. In the subspace spanned by the q degenerate eigenfunction, the matrix elements

$$V_{lm} = \langle \psi_l^{(0)} | V | \psi_m^{(0)} \rangle \quad (9.34)$$

have, in general, diagonal elements V_{ll} and off diagonal elements V_{lm} with $l \neq m$. We can however always use a linear combination $\tilde{\psi}_l^{(0)}$ of the $\psi_m^{(0)}$ that diagonalizes the matrix V_{lm} . In this case follows

$$E_l^{(1)} = \langle \tilde{\psi}_l^{(0)} | V | \tilde{\psi}_l^{(0)} \rangle. \quad (9.35)$$

The easiest way to show this is by writing evaluating the matrix elements of

$$H_0 + V \quad (9.36)$$

with respect to the $\tilde{\psi}_l$ and for $n \leq l, m \leq n+q$ follows

$$\langle \tilde{\psi}_l^{(0)} | H_0 + V | \tilde{\psi}_m^{(0)} \rangle = \left(E_l^{(0)} + \langle \tilde{\psi}_l^{(0)} | V | \tilde{\psi}_l^{(0)} \rangle \right) \delta_{lm} \quad (9.37)$$

If we ignore off diagonal elements to other states, not contained in the degenerate set, we then obtain

$$E_l \simeq E_l^{(0)} + \langle \tilde{\psi}_l^{(0)} | V | \tilde{\psi}_l^{(0)} \rangle \quad (9.38)$$

The above approximation to ignore the coupling to other states is correct to first order in V and we obtain Eq.9.35. If the matrix elements $\langle \tilde{\psi}_l^{(0)} | V | \tilde{\psi}_l^{(0)} \rangle$ are distinct for different l , the degeneracy of the unperturbed problem is completely lifted.

We conclude that the way to determine the eigenvalues of a system with degeneracy corresponds to determining the eigenvalues of the perturbation V_{lm} in an arbitrary basis. In other words, we solve

$$\det \left(V_{lm} - E^{(1)} \delta_{lm} \right) = 0 \quad (9.39)$$

and the eigenvalues $E_l^{(1)}$ of this *secular equation* correspond to the first order corrections to the wave function.

9.2.1 Example 1: two fold degenerate state

We first consider an arbitrary two fold degenerate state. In this case the *secular equation* becomes

$$\begin{vmatrix} V_{11} - E^{(1)} & V_{12} \\ V_{12}^* & V_{22} - E^{(2)} \end{vmatrix} = 0 \quad (9.40)$$

and we obtain the two solutions

$$E^{(1)} = \frac{1}{2} (V_{11} + V_{22} \pm \delta E) \quad (9.41)$$

where

$$\delta E = \sqrt{(V_{11} - V_{22})^2 + 4|V_{12}|^2}. \quad (9.42)$$

is the difference of the two eigenvalues. Thus, an additional perturbation lifts a twofold degeneracy unless $V_{11} = V_{22}$ and $V_{12} = 0$, i.e. the two states do not mix and the perturbation has identical matrix elements. We can also determine the eigenvectors $(\alpha_{+,1}, \alpha_{+,2})$ and $(\alpha_{-,1}, \alpha_{-,2})$ of the secular matrix. The adequate linear combination of the wave functions is then

$$\tilde{\psi}_{\pm} = \alpha_{\pm,1}\psi_1 + \alpha_{\pm,2}\psi_2 \quad (9.43)$$

where ψ_1 and ψ_2 are the initial degenerate wave functions. It holds

$$\begin{aligned} \alpha_{\pm,1} &= \frac{V_{12}^*}{2|V_{12}|} \left(1 \pm \frac{V_{11} - V_{22}}{\delta E} \right)^{1/2} \\ \alpha_{\pm,2} &= \pm \frac{V_{12}}{2|V_{12}|} \left(1 \pm \frac{V_{22} - V_{11}}{\delta E} \right)^{1/2}. \end{aligned} \quad (9.44)$$

9.2.2 Example 2: Stark Effect

We consider a hydrogen atom in an external electric field E_{el} :

$$H = H_0 + V \quad (9.45)$$

with (assume $e > 0$):

$$V = eE_{\text{el}}z = 2E_{\text{el}}r \cos \theta \quad (9.46)$$

Here H_0 is the Hamiltonian of the hydrogen problem (ignore the spin for simplicity). The unperturbed eigenstates are n^2 -fold degenerate, where n is the principle quantum number of the problem. We consider $n = 2$ and have the four wave functions in the $|nlm\rangle$ notations

$$|200\rangle, |211\rangle, |210\rangle, |21-1\rangle \quad (9.47)$$

In order to analyze the secular equation we have to analyze the matrix elements

$$\langle 2lm | V | 2l'm' \rangle. \quad (9.48)$$

Only two elements survive integration. Diagonal elements all vanish as the potential is odd in z . All elements with different m values vanish by orthogonality of the φ integration. Thus we only need to analyze

$$\begin{aligned} \langle 210 | V | 200 \rangle &= \langle 200 | V | 210 \rangle \\ &= eE_{\text{el}} \int d^3r \psi_{210}(\mathbf{r}) \cos \theta \psi_{200}(\mathbf{r}) \end{aligned} \quad (9.49)$$

It holds

$$\begin{aligned}\psi_{200}(\mathbf{r}) &= \frac{2}{(2a_0)^{3/2}} \left(1 - \frac{r}{2a_0}\right) e^{-r/(2a_0)} Y_{0,0}(\theta, \varphi) \\ \psi_{2,1,0}(\mathbf{r}) &= \frac{1}{\sqrt{3}} \frac{1}{(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/(2a_0)} Y_{1,0}(\theta, \varphi)\end{aligned}\quad (9.50)$$

where $Y_{1,0} = \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos\theta$ and $Y_{0,0} = \frac{1}{2\sqrt{\pi}}$. Thus, it follows

$$\begin{aligned}\langle 210 | V | 200 \rangle &= eE_{\text{el}} \frac{1}{2\pi (2a_0)^3} \int_0^\infty r^2 dr \frac{r}{a_0} \left(1 - \frac{r}{2a_0}\right) e^{-r/a_0} \\ &\quad \times \int_0^{2\pi} d\varphi \times \int_0^\pi \sin\theta d\theta \cos^2\theta\end{aligned}\quad (9.51)$$

This gives with $\rho = r/a_0$ and $x = \cos\theta$

$$\langle 210 | V | 200 \rangle = eE_{\text{el}} \frac{a_0}{32\pi} \int_0^\infty d\rho \rho^4 (2 - \rho) e^{-\rho} \int_0^{2\pi} d\varphi \int_{-1}^1 dx x^2 \quad (9.52)$$

It holds

$$\begin{aligned}\int_0^\infty d\rho \rho^4 (2 - \rho) e^{-\rho} &= -72 \\ \int_{-1}^1 dx x^2 &= \frac{2}{3}\end{aligned}\quad (9.53)$$

and we obtain

$$\langle 210 | V | 200 \rangle = -eE_{\text{el}} \frac{a_0}{16} \frac{2}{3} 72 = -3eE_{\text{el}} a_0 \equiv -\Delta \quad (9.54)$$

The secular equation is then

$$\begin{vmatrix} -E^{(1)} & 0 & -\Delta & 0 \\ 0 & -E^{(1)} & 0 & 0 \\ -\Delta & 0 & -E^{(1)} & 0 \\ 0 & 0 & 0 & -E^{(1)} \end{vmatrix} = 0 \quad (9.55)$$

The four eigenvalues are

$$E^{(1)} = 0, 0, \Delta, -\Delta \quad (9.56)$$

Thus, the two states $|211\rangle$ and $|21-1\rangle$ are unaffected by the perturbation and remain doubly degenerate. On the other hand, the two states

$$\frac{1}{\sqrt{2}} (|200\rangle \pm |210\rangle) \quad (9.57)$$

are split. Obviously, the perturbation mixes the $m = 0$ states, while the $m = \pm 1$ states are left degenerate.

Chapter 10

Variational principle

Often it is not possible to find the exact solution of the Schrödinger equation and perturbative approaches are not useful because of the absence of a natural small parameter. In this case one can still approximately determine the ground state energy by minimizing

$$E_v = \langle \phi_v | H | \phi_v \rangle \quad (10.1)$$

with respect to certain variational parameters. Here, $|\phi_v\rangle$ is assumed to be normalized, i.e.

$$\langle \phi_v | \phi_v \rangle = 1. \quad (10.2)$$

The proof of the variational principle is straightforward. We show that for an arbitrary normalized state $|\phi\rangle$ holds that:

$$\langle \phi | H | \phi \rangle \geq E_0 \quad (10.3)$$

where E_0 is the exact ground state energy of H . This follows from the fact that any $|\phi\rangle$ can be expanded w.r.t. the set of eigenfunctions $|\psi_\mu\rangle$ of H :

$$|\phi\rangle = \sum_{\mu} \alpha_{\mu} |\psi_{\mu}\rangle \quad (10.4)$$

such that

$$\langle \phi | H | \phi \rangle = \sum_{\mu} |\alpha_{\mu}|^2 E_{\mu}. \quad (10.5)$$

Here E_{μ} are the eigenvalues of H . Since $\sum_{\mu} |\alpha_{\mu}|^2 = 1$, the mean value of the energy in $|\phi\rangle$ cannot be smaller than its smallest possible value, yielding Eq.10.3.

Using this result one typically starts from an educated guess of the wave function

$$\phi_v(\mathbf{r}) = \phi_v(\lambda_i; \mathbf{r}) \quad (10.6)$$

where λ_i is a set of variational parameters that characterize our guess. We then determine λ_i by minimizing

$$E_v(\lambda_i) = \langle \phi_v | H | \phi_v \rangle. \quad (10.7)$$

Thus, the quality of the wave function is judged by how close it comes to the ground state.

Often one expands the trial wave function w.r.t. a known set of functions and considers the expansion coefficients as variational parameters.

$$|\phi_v\rangle = \sum_{\mu=1}^q \alpha_{\mu} |\varphi_{\mu}\rangle \quad (10.8)$$

The approximation is now that the Hilbert space is assumed to have finite dimension. The variational value for the ground state is then naturally the smallest eigenvalue of the matrix

$$H_{\mu\nu} = \langle \varphi_{\mu} | H | \varphi_{\nu} \rangle \quad (10.9)$$

i.e. we have to solve

$$\det(E\delta_{\mu\nu} - H_{\mu\nu}) = 0. \quad (10.10)$$

If the wave functions are not orthogonal this can easily be generalized to

$$\det(E \langle \psi_{\mu} | \psi_{\nu} \rangle - H_{\mu\nu}) = 0. \quad (10.11)$$

where $\langle \psi_{\mu} | \psi_{\nu} \rangle$ is the overlap integral.

Example 1: harmonic oscillator We start from the harmonic oscillator and make the guess

$$\phi_v(x) = \left(\frac{2\lambda}{\pi}\right)^{1/4} \exp(-\lambda x^2) \quad (10.12)$$

where λ is the variational parameter.

It holds

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \phi_v(x) = -\frac{\hbar^2}{2m} 2\lambda (2\lambda x^2 - 1) \phi_v(x) \quad (10.13)$$

which leads to

$$\langle T \rangle_v = -\frac{\hbar^2}{2m} \int \phi_v(x)^* \frac{d^2}{dx^2} \phi_v(x) dx = \frac{\hbar^2}{2m} \lambda \quad (10.14)$$

On the other hand follows

$$\langle V \rangle_v = \frac{m\omega^2}{2} \int \phi_v(x)^* x^2 \phi_v(x) dx = \frac{m\omega^2}{2} \frac{1}{4\lambda} \quad (10.15)$$

It follows

$$E_v(\lambda) = \frac{\hbar^2}{2m} \lambda + \frac{m\omega^2}{2} \frac{1}{4\lambda} = \hbar\omega \left(\frac{\hbar}{2m\omega} \lambda + \frac{m\omega}{2\hbar} \frac{1}{4\lambda} \right). \quad (10.16)$$

Thus we may as well minimize the energy w.r.t.

$$\mu = \frac{\hbar}{m\omega} \lambda \quad (10.17)$$

since

$$E_v(\mu) = \frac{\hbar\omega}{2} \left(\mu + \frac{1}{4\mu} \right) \quad (10.18)$$

It holds

$$\frac{\partial E_v(\mu)}{\partial \mu} = \frac{\hbar\omega}{2} \left(1 - \frac{1}{\mu^2 4} \right) = 0 \quad (10.19)$$

which gives $\mu_{\min} = \pm \frac{1}{2}$. Only $\mu > 0$ (i.e. $\lambda > 0$ corresponds to a normalized wave function). It follows

$$E_v(\mu_{\min}) = \frac{\hbar\omega}{2} \quad (10.20)$$

which is even the exact result. This is no surprise as the exact wave function is a Gaussian. The wave function is then given as

$$\phi_v(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar} x^2\right). \quad (10.21)$$

We obtain the exact result. It is generally true that the exact ground state is reproduced if it can be expressed in terms of the variational guess for a specific set of parameters. Had we decided for $\phi_v(x) = A \exp(-\lambda x^4)$, we would not have obtained the exact result.

Example 2: double minimum

We have a particle in a potential

$$V(x) = \frac{k}{8a_0^2} (x^2 - a_0^2)^2 \quad (10.22)$$

Here the pre-factor is chosen such that

$$V(x \simeq \pm a) \simeq \frac{k}{2} (x \mp a_0)^2 \quad (10.23)$$

Thus, for large a_0 we have two separated harmonic oscillators. A reasonable variational ansatz is then

$$\phi_v(x) = \alpha (\psi_0(x - a_0) \pm \psi_0(x + a_0)) \quad (10.24)$$

with ground state energy of the harmonic oscillator

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar} x^2\right). \quad (10.25)$$

Here, the key variational parameter is discrete, it is the relative sign \pm . We can now evaluate the potential and kinetic energy. It is useful to introduce dimensionless units

$$\xi = \sqrt{\frac{m\omega}{\hbar}} x = \frac{x}{l_0} \quad (10.26)$$

and then

$$\psi_0(\xi) = \pi^{-1/4} \exp(-\xi^2/2) \quad (10.27)$$

such that $\int \psi_0(\xi)^2 d\xi = 1$. Then

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} &= -\frac{\hbar^2}{2m} \frac{m\omega}{\hbar} \frac{d^2}{d\xi^2} = -\frac{\hbar\omega}{2} \frac{d^2}{d\xi^2} \\ V(\xi) &= \frac{\hbar\omega}{2} \frac{1}{4\rho^2} (x^2 - \rho^2)^2 \end{aligned} \quad (10.28)$$

where $\rho = a_0/l_0$.

It follows for the variational wave function

$$\phi_v(\xi) = \alpha (\psi_0(\xi - \rho) \pm \psi_0(\xi + \rho)) \quad (10.29)$$

The normalization is then

$$\begin{aligned} \int d\xi \phi_v(\xi)^2 &= 2\alpha^2 \left(1 \pm \int d\xi \psi_0(\xi - \rho) \psi_0(\xi + \rho) \right) \\ &= 2\alpha^2 (1 \pm e^{-\rho^2}) \end{aligned} \quad (10.30)$$

which gives

$$\alpha = \frac{1}{\sqrt{2} (1 \pm e^{-\rho^2})^{1/2}}. \quad (10.31)$$

For the Kinetic energy follows

$$\langle \phi_v | T | \phi_v \rangle = \frac{\hbar\omega}{2} \alpha^2 2 \left(\left\langle \psi_+ \left| \frac{d^2}{d\xi^2} \right| \psi_+ \right\rangle \pm \left\langle \psi_+ \left| \frac{d^2}{d\xi^2} \right| \psi_- \right\rangle \right) \quad (10.32)$$

It holds $\langle \psi_+ | T | \psi_+ \rangle = \langle \psi_- | T | \psi_- \rangle = \frac{1}{2}$ and $\langle \psi_+ | T | \psi_- \rangle = \frac{1}{2} e^{-\rho^2} (2\rho^2 - 1)$ such that

$$\langle \phi_v | T | \phi_v \rangle = \frac{\hbar\omega}{4} \frac{1 \pm e^{-\rho^2} (2\rho^2 - 1)}{1 \pm e^{-\rho^2}} \quad (10.33)$$

The potential energy is

$$\langle \phi_v | V | \phi_v \rangle = \frac{\hbar\omega}{2} \frac{\alpha^2}{2\rho^2} \left(\left\langle \psi_+ \left| (\xi^2 - \rho^2)^2 \right| \psi_+ \right\rangle \pm \left\langle \psi_+ \left| (\xi^2 - \rho^2)^2 \right| \psi_- \right\rangle \right) \quad (10.34)$$

It holds

$$\begin{aligned} \left\langle \psi_+ \left| (\xi^2 - \rho^2)^2 \right| \psi_+ \right\rangle &= 2\rho^2 - \frac{3}{4} \\ \left\langle \psi_+ \left| (\xi^2 - \rho^2)^2 \right| \psi_- \right\rangle &= e^{-\rho^2} \left(\rho^4 - \rho^2 + \frac{3}{4} \right) \end{aligned} \quad (10.35)$$

and we find:

$$\langle \phi_v | V | \phi_v \rangle = \frac{\hbar\omega}{4} \left(\frac{1 - \frac{3}{8\rho^2} \pm \frac{1}{2} e^{-\rho^2} \left(\rho^2 - 1 + \frac{3}{4\rho^2} \right)}{1 \pm e^{-\rho^2}} \right) \quad (10.36)$$

It then follows for the variational energy

$$E_v = \frac{\hbar\omega}{2} \frac{1 - \frac{3}{16\rho^2} \pm e^{-\rho^2} \left(\frac{5}{4}\rho^2 - \frac{3}{4} + \frac{3}{16\rho^2} \right)}{1 \pm e^{-\rho^2}} \quad (10.37)$$

This function is easily analyzed graphically. The relevant regime is $\rho > 1$. For $1 < \rho < 1.065$ is the energy of the positive sign lower. For $\rho > 1.065$ is the wave function with negative sign is lower in energy. For large ρ is the energy gain of the negative solution

$$\Delta E = \frac{\hbar\omega}{2} \frac{5}{4} \rho^2 e^{-\rho} \quad (10.38)$$

i.e. it is exponentially small as it is a result of the overlap of the two wave functions.

Example 3: Hydrogen molecule

We consider the hydrogen molecule H_2^+ , i.e. a molecule with two nuclei and one electron. The Hamiltonian is

$$H = \frac{\hat{p}^2}{2m} + \frac{e^2}{R} - \frac{e^2}{r_1} - \frac{e^2}{r_2} \quad (10.39)$$

where $r_1 = |\mathbf{r} - \mathbf{R}_1|$ and $r_2 = |\mathbf{r} - \mathbf{R}_2|$ is the distance of the electrons from the first and second nucleus, respectively. $R = |\mathbf{R}_1 - \mathbf{R}_2|$ is the distance between the two nuclei.

A natural ansatz for the ground state is

$$|\phi_v\rangle = \alpha_1 |\psi_1\rangle + \alpha_2 |\psi_2\rangle \quad (10.40)$$

where

$$\psi_i(\mathbf{r}) = \langle \mathbf{r} | \psi_i \rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_i/a_0} \quad (10.41)$$

is the ground state of the hydrogen atom centered around \mathbf{R}_i . The variational parameters are the coefficients α_i and the distance between the nuclei R . We first need to determine the eigenvalues of the matrix

$$\begin{pmatrix} H_{11} - E & H_{12} - E \langle \psi_1 | \psi_2 \rangle \\ H_{21} - E \langle \psi_1 | \psi_2 \rangle^* & H_{22} - E \end{pmatrix} \quad (10.42)$$

It holds $H_{11} = H_{22}$ and $H_{12} = H_{21}$, which gives

$$\begin{aligned} E_+ &= \frac{H_{11} + H_{12}}{1 + \Delta_{12}} \\ E_- &= \frac{H_{11} - H_{12}}{1 - \Delta_{12}} \end{aligned} \quad (10.43)$$

with eigenvectors

$$\begin{aligned} |\phi_+\rangle &= N (|\psi_1\rangle + |\psi_2\rangle) \\ |\phi_-\rangle &= N (|\psi_1\rangle - |\psi_2\rangle) \end{aligned} \quad (10.44)$$

We only need to determine

$$\begin{aligned} I &= -e^2 \left\langle \psi_1 \left| \frac{1}{r_2} \right| \psi_1 \right\rangle \\ K &= -e^2 \left\langle \psi_1 \left| \frac{1}{r_1} \right| \psi_2 \right\rangle \end{aligned} \quad (10.45)$$

and obtain

$$\begin{aligned} E_+ &= E_H + \frac{e^2}{R} + \frac{I - K}{1 + \Delta} \\ E_- &= E_H + \frac{e^2}{R} + \frac{I + K}{1 - \Delta} \end{aligned} \quad (10.46)$$

where E_H is the ground state energy of the Hydrogen atom. It follows from a numerical evaluation of the matrix elements that $I, K < 0$ and that E_+ is lower than E_- .

There exists another, physically very appealing formulation of quantum mechanics invented by Richard Feynman. The idea is very simple: If we consider a double slit experiment we would have a source and a screen to detect the signal. The probability amplitude to hit the screen is then the sum over the amplitude of the two paths:

$$A(\text{source} \rightarrow \text{screen}) = \sum_{i=1}^2 \mathcal{A}(\text{source} \rightarrow s_i \rightarrow \text{screen}) \quad (10.47)$$

This idea can be generalized to many slits and many screens, and the idea is to consider every potential as a superposition of slits and screens.

Chapter 11

Path integral formulation of quantum mechanics

The physical picture behind the path integral approach is that one can achieve a correct reformulation of quantum mechanics in terms of interfering classical paths. When we discuss a double slit experiment, we usually draw two classical paths, one where the particle goes through the upper and one where it goes through the lower slit. After the scattering at the slit potential the interference between such paths is considered. The spirit of the path integral approach is to describe each potential and an sum of many multiple-slit setups. We then consider all possible interference pattern, which eventually determine matrix elements and expectation values. The path integral is therefore a formulation of quantum mechanics that can be achieved without introducing operators. It also makes very direct contact to the classical limit. While path integrals are not the most efficient tools to solve generic problems of single particle quantum mechanics, their generalization to functional integrals in quantum field theories turn out to be extremely useful.

The time evolution of a quantum state is given by

$$|\psi(t)\rangle = e^{-i\frac{Ht}{\hbar}} |\psi\rangle. \quad (11.1)$$

It is therefore interesting to analyze the transitions from an initial state to a final state, or to ask what is the probability that a particle at time $t = T$ is in state $|\psi_f\rangle$ under the condition that it was in a state $|\psi_i\rangle$ at $t = 0$. This information is given by

$$\langle \psi_f | e^{-i\frac{HT}{\hbar}} | \psi_i \rangle. \quad (11.2)$$

To be specific we analyze the case where $|\psi_i\rangle$ and $|\psi_f\rangle$ are eigenstates of the position operator

$$\langle x_f | e^{-i\frac{HT}{\hbar}} | x_i \rangle. \quad (11.3)$$

If

$$H = T + V \quad (11.4)$$

it holds in general that

$$e^{-i\frac{Ht}{\hbar}} \neq e^{-i\frac{Tt}{\hbar}} e^{-i\frac{Vt}{\hbar}}. \quad (11.5)$$

However, for very small time steps one can write

$$e^{-i\frac{Ht}{\hbar}} = e^{-i\frac{Tt}{\hbar}} e^{-i\frac{Vt}{\hbar}} + \mathcal{O}(t^2). \quad (11.6)$$

To see this we expand both sides in a Taylor series and compare:

$$\begin{aligned} 1 - i\frac{Ht}{\hbar} + \mathcal{O}(t^2) &= \left(1 - i\frac{Tt}{\hbar}\right) \left(1 - i\frac{Vt}{\hbar}\right) + \mathcal{O}(t^2) \\ &\simeq 1 - i\frac{(T+V)t}{\hbar} + \mathcal{O}(t^2). \end{aligned} \quad (11.7)$$

Thus, the trick is to introduce small time steps $\delta t = T/N$ and consider the evolution during those short times

$$e^{-i\frac{HT}{\hbar}} = \left(e^{-i\frac{H\delta t}{\hbar}}\right)^N. \quad (11.8)$$

Then, we can write

$$e^{-i\frac{H\delta t}{\hbar}} = e^{-i\frac{T\delta t}{\hbar}} e^{-i\frac{V\delta t}{\hbar}} + \mathcal{O}\left((\delta t)^2\right). \quad (11.9)$$

The transition amplitude can now be written as:

$$\langle x_f | e^{-i\frac{HT}{\hbar}} | x_i \rangle = \langle x_f | e^{-i\frac{H\delta t}{\hbar}} e^{-i\frac{H\delta t}{\hbar}} \dots e^{-i\frac{H\delta t}{\hbar}} | x_i \rangle. \quad (11.10)$$

We next introduce a complete set of states for each intermediate time slice:

$$1 = \int dx_j |x_j\rangle \langle x_j|. \quad (11.11)$$

Then

$$\begin{aligned} \langle x_f | e^{-i\frac{HT}{\hbar}} | x_i \rangle &= \int \prod_{j=1}^{N-1} dx_j \langle x_f | e^{-i\frac{H\delta t}{\hbar}} | x_{N-1} \rangle \langle x_{N-1} | e^{-i\frac{H\delta t}{\hbar}} | x_{N-2} \rangle \\ &\quad \times \dots \langle x_2 | e^{-i\frac{H\delta t}{\hbar}} | x_1 \rangle \langle x_1 | e^{-i\frac{H\delta t}{\hbar}} | x_i \rangle \end{aligned} \quad (11.12)$$

If $x_i = x_0$ and $x_f = x_N$, it follows:

$$\langle x_f | e^{-i\frac{HT}{\hbar}} | x_i \rangle = \int \left(\prod_{j=1}^{N-1} dx_j \right) \prod_{j=0}^{N-1} \langle x_{j+1} | e^{-i\frac{H\delta t}{\hbar}} | x_j \rangle. \quad (11.13)$$

We need to analyze the matrix elements for small δt :

$$\begin{aligned} \langle x_{j+1} | e^{-i\frac{H\delta t}{\hbar}} | x_j \rangle &\simeq \langle x_{j+1} | e^{-i\frac{T\delta t}{\hbar}} e^{-i\frac{V\delta t}{\hbar}} | x_j \rangle \\ &= \langle x_{j+1} | e^{-i\frac{T\delta t}{\hbar}} | x_j \rangle e^{-i\frac{V(x_j)\delta t}{\hbar}}. \end{aligned} \quad (11.14)$$

Furthermore, it holds for the kinetic energy matrix element:

$$\begin{aligned}\langle x_{j+1} | e^{-i\frac{T\delta t}{\hbar}} | x_j \rangle &= \int dp \langle x_{j+1} | e^{-i\frac{T\delta t}{\hbar}} | p \rangle \langle p | x_j \rangle \\ &= \int dp \langle x_{j+1} | p \rangle \langle p | x_j \rangle e^{-i\frac{T(p)\delta t}{\hbar}}\end{aligned}\quad (11.15)$$

Since $\langle x_{j+1} | p \rangle = \frac{\exp(i\frac{p x_{j+1}}{\hbar})}{2\pi}$ it follows:

$$\langle x_{j+1} | e^{-i\frac{T\delta t}{\hbar}} | x_j \rangle = \int \frac{dp}{2\pi} e^{-\frac{i}{\hbar}(T(p))\delta t} e^{i\frac{p}{\hbar}(x_{j+1}-x_j)}.\quad (11.16)$$

The integral over p is known as a Gaussian integral

$$\int_{-\infty}^{\infty} dp e^{i\frac{\alpha}{2}p^2} = \int_0^{\infty} dz \frac{e^{i\frac{\alpha}{2}z}}{\sqrt{z}} = \sqrt{\frac{2\pi i}{\alpha}}\quad (11.17)$$

which follows from

$$\int_{-\infty}^{\infty} dp e^{-\frac{\alpha}{2}p^2} = \sqrt{\frac{2\pi i}{\alpha}}\quad (11.18)$$

which is convergent for $\text{Re}\alpha > 0$. We then write $\alpha = ia + \eta$ and set $\eta \rightarrow 0$ at the end. It follows

$$\langle x_{j+1} | e^{-i\frac{T\delta t}{\hbar}} | x_j \rangle = \left(\frac{m}{2\pi i \hbar \delta t}\right)^{1/2} e^{i\delta t \frac{m}{2} \left(\frac{x_{j+1}-x_j}{\delta t}\right)^2}.\quad (11.19)$$

Then follows with the abbreviation

$$\int Dx \cdots = \left(\frac{m}{2\pi i \hbar \delta t}\right)^{N/2} \int \prod_{j=1}^{N-1} dx_j \cdots\quad (11.20)$$

that

$$\langle x_f | e^{-i\frac{HT}{\hbar}} | x_i \rangle = \int Dx \prod_{j=0}^{N-1} e^{i\delta t \frac{m}{2} \left(\frac{x_{j+1}-x_j}{\delta t}\right)^2 - i\frac{V(x_j)\delta t}{\hbar}}.\quad (11.21)$$

If we perform the limit $\delta t \rightarrow 0$ we can write

$$\langle x_f | e^{-i\frac{HT}{\hbar}} | x_i \rangle = \int Dx e^{\frac{i}{\hbar}S[x]},\quad (11.22)$$

where

$$S[x] = \int_0^T dt \left(\frac{m}{2}\dot{x}^2 - V(x)\right)\quad (11.23)$$

is the classical action.

A path from x_i to x_f can be written as

$$x(t) = x_{\text{cl}}(t) + \delta x(t)\quad (11.24)$$

where $x_{\text{cl}}(t)$ is the classical path, as obtained from

$$\frac{\delta S}{\delta x} = 0 \quad (11.25)$$

which corresponds to

$$m \frac{d^2 x_{\text{cl}}(t)}{dt^2} = - \frac{\partial V(x_{\text{cl}})}{\partial x_{\text{cl}}}. \quad (11.26)$$

In case of a free particle it holds for example

$$x_{\text{cl}}(t) = x_i + \frac{t}{T} (x_f - x_i). \quad (11.27)$$

yielding the classical action $S[x_{\text{cl}}] = \frac{m}{2} \frac{(x_f - x_i)^2}{T}$.

For the *quantum fluctuations* $\delta x(t)$ follows obviously that

$$\delta x(0) = \delta x(T) = 0. \quad (11.28)$$

Inserting this decomposition into the action gives

$$\begin{aligned} T[x] &= \int_0^T dt \frac{m}{2} \dot{x}^2 = \int_0^T dt \frac{m}{2} \dot{x}_{\text{cl}}^2 + \int_0^T dt \frac{m}{2} (\delta \dot{x})^2 \\ &\quad + m \int_0^T dt \dot{x}_{\text{cl}} \delta \dot{x}. \end{aligned} \quad (11.29)$$

The last term gives

$$\begin{aligned} \int_0^T dt \dot{x}_{\text{cl}} \delta \dot{x} &= - \int_0^T dt \frac{d^2 x_{\text{cl}}(t)}{dt^2} \delta x(t) + \dot{x}_{\text{cl}} \delta x|_0^T \\ &= - \int_0^T dt \frac{d^2 x_{\text{cl}}(t)}{dt^2} \delta x(t) \\ &= \int_0^T dt \frac{\partial V(x_{\text{cl}})}{\partial x_{\text{cl}}} \delta x(t) \end{aligned} \quad (11.30)$$

and we obtain

$$\begin{aligned} S[x] &= S_{\text{cl}}[x] + \int_0^T dt \frac{m}{2} (\delta \dot{x})^2 \\ &\quad - \int_0^T dt \left(V(x_{\text{cl}} + \delta x) - V(x_{\text{cl}}) - \frac{\partial V(x_{\text{cl}})}{\partial x_{\text{cl}}} \delta x \right) \end{aligned} \quad (11.31)$$

In case of a smooth potential one can expand

$$V(x_{\text{cl}} + \delta x) \simeq V(x_{\text{cl}}) + \frac{\partial V(x_{\text{cl}})}{\partial x_{\text{cl}}} \delta x + \frac{1}{2} \frac{\partial^2 V(x_{\text{cl}})}{\partial x_{\text{cl}}^2} \delta x^2 \quad (11.32)$$

and the quadratic term is the only that contributes

$$S[x] = S_{\text{cl}}[x] + S_{\text{q}}[x] \quad (11.33)$$

where

$$S_q[x] = \frac{1}{2} \int_0^T dt \left(m (\delta \dot{x})^2 - \frac{\partial^2 V(x_{cl})}{\partial x_{cl}^2} \delta x^2 \right). \quad (11.34)$$

In this limit follows

$$\langle x_f | e^{-i\frac{HT}{\hbar}} | x_i \rangle \simeq e^{\frac{i}{\hbar} S_{cl}[x]} \int Dx e^{\frac{i}{\hbar} S_q[x]} \quad (11.35)$$

and quantum fluctuations enter the theory only through a Gaussian integral.

11.1 Path integral of a free particle

To perform at least once a path integral explicitly, we consider the free particle limit with $V = 0$. It holds

$$\begin{aligned} \langle x_f | e^{-i\frac{HT}{\hbar}} | x_i \rangle &= \int Dx \prod_{j=0}^{N-1} e^{i\delta t \frac{m}{2\hbar} \left(\frac{x_{j+1} - x_j}{\delta t} \right)^2} \\ &= \left(\frac{m}{2\pi i \hbar \delta t} \right)^{N/2} \int dx_1 dx_2 \dots dx_{N-1} e^{i\frac{m\delta t}{2\hbar} \left(\frac{x_N - x_{N-1}}{\delta t} \right)^2} \\ &\times e^{i\frac{m\delta t}{2\hbar} \left(\frac{x_{N-1} - x_{N-2}}{\delta t} \right)^2} \dots e^{i\frac{m\delta t}{2\hbar} \left(\frac{x_2 - x_1}{\delta t} \right)^2} e^{i\frac{m\delta t}{2\hbar} \left(\frac{x_1 - x_0}{\delta t} \right)^2} \end{aligned} \quad (11.36)$$

with

$$x_i = \sqrt{\frac{2\hbar\delta t}{m}} y_i \quad (11.37)$$

follows

$$\begin{aligned} \langle x_f | e^{-i\frac{HT}{\hbar}} | x_i \rangle &= (i\pi)^{-\frac{N}{2}} \sqrt{\frac{m}{2\hbar\delta t}} \int dy_1 dy_2 \dots dy_{N-1} e^{i(y_N - y_{N-1})^2} \\ &\times e^{i(y_{N-1} - y_{N-2})^2} \dots e^{i(y_2 - y_1)^2} e^{i(y_1 - y_0)^2}, \end{aligned} \quad (11.38)$$

where we used

$$\left(\frac{m}{2\pi i \hbar \delta t} \right)^{N/2} \left(\frac{2\hbar\delta t}{m} \right)^{\frac{N-1}{2}} = (i\pi)^{-\frac{N}{2}} \sqrt{\frac{m}{2\hbar\delta t}}. \quad (11.39)$$

It is useful to introduce

$$z_i = y_i - y_{i-1} \quad (11.40)$$

Then follows

$$\begin{aligned} z_1 &= y_1 - y_0 \\ z_2 &= y_2 - y_0 - z_1 \\ z_N &= y_N - y_0 - \sum_{l=1}^{N-1} z_l \end{aligned} \quad (11.41)$$

It holds

$$\begin{aligned}
\int dy_1 e^{i(y_2-y_1)^2} e^{i(y_1-y_0)^2} &= \sqrt{\frac{\pi}{2i}} e^{\frac{i}{2}(y_2-y_0)^2} \\
\int dy_2 e^{i(y_3-y_2)^2} e^{\frac{i}{2}(y_2-y_0)^2} &= \sqrt{\frac{2\pi}{3i}} e^{\frac{i}{3}(y_3-y_0)^2} \\
\int dy_3 e^{i(y_4-y_3)^2} e^{\frac{i}{4}(y_3-y_0)^2} &= \sqrt{\frac{3\pi}{4i}} e^{\frac{i}{4}(y_4-y_0)^2} \\
\int dy_l e^{i(y_{l+1}-y_l)^2} e^{\frac{i}{l+1}(y_l-y_0)^2} &= \sqrt{\frac{l\pi}{(l+1)i}} e^{\frac{i}{4}(y_{l+1}-y_0)^2}, \quad (11.42)
\end{aligned}$$

Which yields

$$\langle x_f | e^{-i\frac{HT}{\hbar}} | x_i \rangle = \sqrt{\frac{m}{2\pi i \hbar N \delta t}} e^{\frac{i}{N}(y_{l+1}-y_0)^2} \quad (11.43)$$

$$= \sqrt{\frac{m}{2\pi i \hbar N \delta t}} \exp\left(i\frac{m}{2\hbar N \delta t} (x_f - x_i)^2\right) \quad (11.44)$$

Using

$$N \delta t = T \quad (11.45)$$

follows finally

$$\langle x_f | e^{-i\frac{HT}{\hbar}} | x_i \rangle = \sqrt{\frac{m}{2\pi i \hbar T}} \exp\left(i\frac{m(x_f - x_i)^2}{2\hbar T}\right). \quad (11.46)$$

We call this transition probability amplitude:

$$G(x_f, x_i, t) = \langle x_f | e^{-i\frac{Ht}{\hbar}} | x_i \rangle \quad (11.47)$$

and it follows

$$\frac{\partial G(x_f, x_i, t)}{\partial t} = \frac{i\hbar}{2m} \frac{\partial^2 G(x_f, x_i, t)}{\partial x_i^2} \quad (11.48)$$

$$i\hbar \frac{\partial G(x_f, x_i, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 G(x_f, x_i, t)}{\partial x_i^2} \quad (11.49)$$

With an arbitrary initial wave function $\psi_i(x)$ follows

$$\begin{aligned}
\psi_f(x, t) &= \langle x | e^{-it} | \psi_i \rangle = \int dx_i \langle x | e^{-i\frac{HT}{\hbar}} | x_i \rangle \langle x_i | \psi_i \rangle \\
&= \int dx_i G(x, x_i, t) \psi_i(x_i) \quad (11.50)
\end{aligned}$$

such that

$$\begin{aligned}
i\hbar \frac{\partial \psi_f(x, t)}{\partial t} &= i\hbar \int dx_i \frac{\partial G(x_f, x_i, t)}{\partial t} \psi_i(x_i) \\
-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_f(x, t)}{\partial x^2} &= -\frac{\hbar^2}{2m} \int dx_i \frac{\partial^2 G(x_f, x_i, t)}{\partial x_i^2} \psi_i(x_i) \quad (11.51)
\end{aligned}$$

Thus, it follows that the wave function generated this way also obeys Schrödinger's equation:

$$i\hbar \frac{\partial \psi_f(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_f(x, t)}{\partial x^2}. \quad (11.52)$$

Chapter 12

Scattering Theory

$$H = H_0 + V \quad (12.1)$$

$$H_0 = \frac{\mathbf{p}^2}{2m} \quad (12.2)$$

$$H_0 |\phi\rangle = E |\phi\rangle \quad (12.3)$$

Want to solve

$$(H_0 + V) |\psi\rangle = E |\psi\rangle \quad (12.4)$$

formally solved by

$$|\psi\rangle = (E - H_0)^{-1} V |\psi\rangle + |\phi\rangle \quad (12.5)$$

need to regularize

$$|\psi^{(\pm)}\rangle = (E \pm i\varepsilon - H_0)^{-1} V |\psi\rangle + |\phi\rangle \quad (12.6)$$

Gives

$$\langle \mathbf{r} | \psi^{(\pm)} \rangle = \langle \mathbf{r} | \phi \rangle + \int d^3 r' \langle \mathbf{r} | (E \pm i\varepsilon - H_0)^{-1} | \mathbf{r}' \rangle \langle \mathbf{r}' | V \psi^{(\pm)} \rangle \quad (12.7)$$

It holds

$$\langle \mathbf{r} | \phi \rangle = \frac{e^{i\mathbf{k}\cdot\mathbf{x}}}{(2\pi)^{3/2}} \quad (12.8)$$

$$G_{\pm}(\mathbf{r}, \mathbf{r}') = \frac{\hbar^2}{2m} \langle \mathbf{r} | (E \pm i\varepsilon - H_0)^{-1} | \mathbf{r}' \rangle \quad (12.9)$$

$$= -\frac{1}{4\pi} \frac{e^{\pm ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \quad (12.10)$$

Gives

$$\psi^{(\pm)}(\mathbf{r}) = \phi(\mathbf{r}) - \frac{2m}{\hbar^2} \int d^3 r' \frac{e^{\pm ik|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|} V(\mathbf{r}') \psi^{(\pm)}(\mathbf{r}') \quad (12.11)$$

If $r = |\mathbf{r}| \gg r' = |\mathbf{r}'|$ follows with

$$\mathbf{k}' = k \frac{\mathbf{r}}{r} \quad (12.12)$$

that

$$\psi^{(+)}(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} \left(e^{i\mathbf{k}\cdot\mathbf{r}} + \frac{e^{ikr}}{r} f(\mathbf{k}', \mathbf{k}) \right) \quad (12.13)$$

where the scattering amplitude is

$$f(\mathbf{k}', \mathbf{k}) = -\frac{2m}{\hbar^2} \sqrt{\frac{\pi}{2}} \int d^3r' e^{-i\mathbf{k}\cdot\mathbf{r}'} V(\mathbf{r}') \psi^{(+)}(\mathbf{r}') \quad (12.14)$$

The differential cross section $\frac{d\sigma}{d\Omega}$. Consider a large number of identically prepared particles all characterized by a free particle wave function. What is the number of incident particles crossing a plane perpendicular to the incident direction per unit area per unit time? This is just the probability flux due to the first term. What is the number of scattered particles going into a small area $d\sigma$ around a differential solid angle element $d\Omega$?

$$\begin{aligned} \frac{d\sigma}{d\Omega} d\Omega &= \frac{\# \text{ particles scattered into } d\Omega \text{ per unit time}}{\# \text{ of incident particles crossing unit area per unit time}} \\ &= \frac{r^2 |\mathbf{j}_{scatt}|}{|\mathbf{j}_{incid}|} = |f(\mathbf{k}', \mathbf{k})|^2 d\Omega \end{aligned} \quad (12.15)$$

If $V(\mathbf{r}) = V(r)$ follows that $f(\mathbf{k}', \mathbf{k})$ is only a function of $|\mathbf{k}' - \mathbf{k}| \equiv q = 2k \sin \frac{\theta}{2}$ where θ is the angle between incoming and outgoing momentum. Thus we obtain

$$\psi^{(+)}(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} \left(e^{i\mathbf{k}\cdot\mathbf{r}} + \frac{e^{ikr}}{r} f(\theta) \right) \quad (12.16)$$