Chapter 2

Time–Dependent Schrödinger Equation

2.1 Wave Function and Time–Dependent Schrödinger Equation

In Chapt.1 we discussed how to understand the wave–particle duality. According to Planck and Einstein the energy and frequency of light are related by $E = \hbar\omega$. De Broglie extended this dualism to massive particles by relating in addition the momentum to the wave vector $p = \hbar k$.

It was Erwin Schrödinger who reconsidered de Broglie's matter waves and discovered in 1926 a wave equation, the equation of motion corresponding to the wave nature of particles, which fits the physical observations. This differential equation is a fundamental equation and cannot be derived from first principles but we can make its form plausible.

Let us consider plane waves or rather wave packets which are of the form

$$\psi(t,x) = e^{i(kx-\omega t)} \tag{2.1}$$

$$\psi(t,x) = \int_{-\infty}^{\infty} \frac{dk}{\sqrt{2\pi}}\, \tilde{\psi}(k)\, e^{i(kx-\omega t)} \quad . \tag{2.2}$$

We differentiate these waves with respect to t and x and recall the relations of wave and particle properties, Eq. (1.22)

$$i\hbar \frac{\partial}{\partial t}\psi(t,x) = \underbrace{\hbar\omega}_{E}\psi = E\,\psi \quad \rightarrow \quad \int \frac{dk}{\sqrt{2\pi}}\, \underbrace{\hbar\omega}_{E}\, \tilde{\psi}(k)\, e^{i(kx-\omega t)} \tag{2.3}$$

$$-i\hbar\,\nabla\psi(t,x) = \underbrace{\hbar k}_{p}\,\psi = p\,\psi \quad \rightarrow \quad \int \frac{dk}{\sqrt{2\pi}}\, \underbrace{\hbar k}_{p}\, \tilde{\psi}(k)\, e^{i(kx-\omega t)} \tag{2.4}$$

$$-\hbar^2\,\Delta\psi(t,x) = \underbrace{(\hbar k)^2}_{p^2}\,\psi = p^2\,\psi \quad \rightarrow \quad \int \frac{dk}{\sqrt{2\pi}}\, \underbrace{(\hbar k)^2}_{p^2}\, \tilde{\psi}(k)\, e^{i(kx-\omega t)} \quad . \tag{2.5}$$

The nonrelativistic energy–momentum relation for massive particles, where we assume for simplicity that the potential $V = V(x)$ is independent of time

$$E = \frac{p^2}{2m} + V(x)\,, \tag{2.6}$$

then provides a differential equation for ψ which Schrödinger assumed to hold quite generally for massive particles in an external potential $V(x)$[1].

Proposition 2.1.1 (Time-dependent Schrödinger equation)

$$i\hbar\,\frac{\partial}{\partial t}\,\psi\,(t,x) \;=\; \Big(-\tfrac{\hbar^2}{2m}\,\Delta \;+\; V(x)\Big)\,\psi\,(t,x) \;=\; H\,\psi\,(t,x)$$

The operator $H = -\frac{\hbar^2}{2m}\,\Delta + V(x)$ is called the *Hamiltonian* of the system, $\hbar$ is Planck's constant and m is the mass of the particle.

The solution $\psi(t,x)$ of the Schrödinger equation is called the *wave function*. It contains all the information about a physical system. The physical interpretation of the wave function is due to Max Born (see Prop. 1.7.1) and can be phrased in the following way: The probability for finding the particle in an interval $[x, x+dx]$ is given by $|\psi(t,x)|^2 dx$, which we have illustrated in Fig. 2.1.

Remark I: In deducing the Schrödinger equation within plane waves and wave packets we see that we can assign operators to the physical quantities energy and momentum

$$i\hbar\,\frac{\partial}{\partial t}\,\psi \;=\; E\,\psi \quad \text{and} \quad -\,i\hbar\,\nabla\,\psi \;=\; p\,\psi\,. \tag{2.7}$$

This *quantum mechanical correspondence* between physical quantities and operators

$$E \;\;\rightarrow\;\; i\hbar\,\frac{\partial}{\partial t} \quad \text{and} \quad p \;\;\rightarrow\;\; -i\hbar\,\nabla \tag{2.8}$$

is quite generally valid (when applied to any wave function). To classical relations correspond quantum mechanical ones. Thus we can quickly find the Schrödinger equation by starting with the classical Hamilton function $H(x,p) = \frac{p^2}{2m} + V = E$. We substitute Eq. (2.8), get exactly the Hamilton–operator H which applied to a wave function represents the Schrödinger equation.

[1]Historically, Schrödinger who was informed by Einstein about de Broglie's thesis gave a talk at the ETH Zürich in 1925. There Debye encouraged him to look for a wave equation and Schrödinger indeed found quickly one, nowadays known as Klein-Gordon equation, by using the relativistic energy–momentum relation, which however did not reproduce the spectrum of the H-atom correctly. During his Christmas vacations in a Pension near Arosa Schrödinger tried again by working now with nonrelativistic relations and discovered the successful "Schrödinger equation" which describes the spectrum correctly.

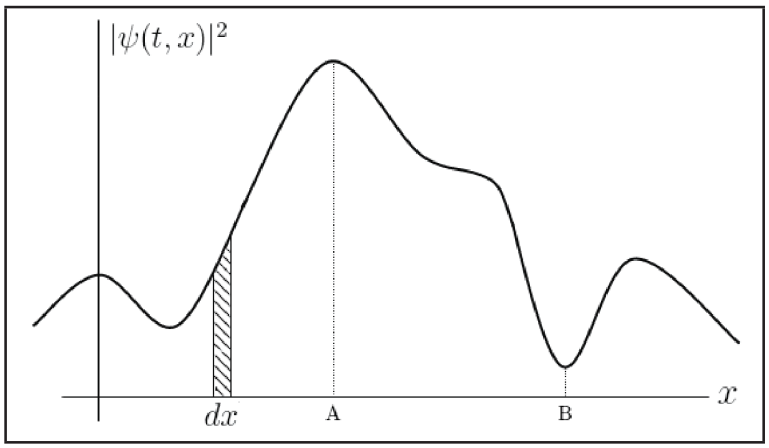

Figure 2.1: Probability interpretation of the wave function: The probability of finding the particle in the interval dx is given by the striped area. The probability to find the particle at location A is highest, whereas it is lowest for location B.

Remark II: The statistical interpretation of the wave function leads to a principal uncertainty to localize a particle. We cannot predict the definite measurement outcome for a specific particle, where it is localized at a certain time, thus we cannot assign a path to the particle.

Since we want to associate the wave function with a single particle, it is reasonable to require the probability to find the electron anywhere in space to be exactly equal to one. Since this may not be the case for all ψ a priori, we introduce a *normalization* condition:

$$\int_{-\infty}^{\infty} dx\, |\psi(t,x)|^2 = 1\,. \tag{2.9}$$

The normalization thus imposes a condition on the wave function, namely on it's asymptotic behaviour, i.e. for $|x| \to \infty$:

$$\text{1-dim.} \quad |\psi(t,x)| \leq \frac{const.}{|x|^{\frac{1}{2}+\epsilon}} \qquad \text{3-dim.} \quad |\psi(t,\vec{x})| \leq \frac{const.}{|\vec{x}|^{1+\epsilon}}\,. \tag{2.10}$$

In other words, the wave function must be a square integrable function

$$\psi(t,x) \in L_2 \quad \text{space of all square integrable functions}\,. \tag{2.11}$$

We conclude that formal solutions of the Schrödinger equation, that are not normalizable, have no physical meaning in this context.

Example: Plane waves $e^{i(kx-\omega t)}$ are solutions of the Schrödinger equation, which can only be normalized in a box. For a box of length L we write

$$\begin{aligned} \psi(t,x) &= \frac{1}{\sqrt{L}}\, e^{i(kx-\omega t)} \qquad \text{for } 0 \le x \le L \\ \psi(t,x) &= 0 \qquad\qquad\qquad\quad \text{outside of box} \end{aligned} \tag{2.12}$$

$$\Rightarrow \quad \int_{-\infty}^{\infty} dx\, \psi^*(t,x)\psi(t,x) \;=\; \frac{1}{L}\int_0^L dx\, \underbrace{e^{-i(kx-\omega t)}\, e^{i(kx-\omega t)}}_{1} = \frac{L}{L} = 1\,. \tag{2.13}$$

So we conclude that plane waves can only represent particles in a box, quite generally we need wave packets for their description.

Résumé:
The Schrödinger equation is a partial differential equation with the following properties:

1. 1^{st} **order in time** t: the wave function is determined by initial conditions, which is desirable from a physical point of view,
2. **linear in** ψ: $\Rightarrow$ superposition principle: linear combinations of solutions are again solutions, i.e. if ψ_1, ψ_2 are solutions $\Rightarrow \psi = c_1\psi_1 + c_2\psi_2$ with $c_1, c_2 \in \mathbb{C}$ is a solution,
3. **homogen**: the normalization holds for all times t.

2.2 Continuity Equation

With the probability density $|\psi(t,\vec{x})|^2$ we can associate a current density $\vec{j}(t,\vec{x})$ analogously to the charge density in electrodynamics. These densities will satisfy a continuity equation.

Let us start from the time dependent Schrödinger equation in 3 dimensions

$$i\hbar\frac{\partial}{\partial t}\,\psi(t,\vec{x}) \;=\; H\,\psi(t,\vec{x}) \tag{2.14}$$

and form it's complex conjugate, where we use that the Hamiltonian H is a hermitian operator, which, in the present context[2], means that $H = H^*$, to gain

$$-i\hbar\frac{\partial}{\partial t}\,\psi^*(t,\vec{x}) \;=\; H\,\psi^*(t,\vec{x})\,. \tag{2.15}$$

[2] A mathematically more precise formulation of this criterion will be given later in Sec. 2.3

Definition 2.1 *The **probability density** ρ is given by the modulus squared of the wave function ψ*

$$\rho(t,\vec{x}) \;:=\; |\psi(t,\vec{x})|^2 \;=\; \psi^*\psi(t,\vec{x}) \;\;.$$

Performing the derivative of the probability density ρ with respect to time, we get

$$\frac{\partial}{\partial t}\,\rho(t,\vec{x}) \;=\; \frac{\partial}{\partial t}\,\psi^*\psi(t,\vec{x}) \;=\; \dot{\psi}^*\psi \;+\; \psi^*\dot{\psi}\,, \tag{2.16}$$

where we have used the notation $\frac{\partial}{\partial t}\,\psi \;=\; \dot{\psi}$. Inserting the Schrödinger equation (2.14) and its complex conjugate (2.15) into Eq. 2.16 we find

$$\begin{aligned}
\dot{\rho}(t,\vec{x}) \;&=\; -\frac{1}{i\hbar}\,[\,(H\,\psi^*)\,\psi \;-\; \psi^* H\psi\,] \;= \\
&=\; \frac{\hbar}{2mi}\,[\,(\Delta\psi^*)\,\psi \;-\; \psi^*\Delta\psi\,] \;-\; \frac{1}{i\hbar}[\,V\psi^*\psi \;-\; \underbrace{\psi^* V\psi}_{V\psi^*\psi}\,] \;= \\
&=\; \frac{\hbar}{2mi}\,\vec{\nabla}\,[\,(\vec{\nabla}\psi^*)\psi \;-\; \psi^*\vec{\nabla}\psi\,]\,.
\end{aligned} \tag{2.17}$$

Definition 2.2 *We define the **probability current** $\vec{j}$ as*

$$\vec{j}(t,\vec{x}) \;:=\; \tfrac{\hbar}{2mi}\,[\,\psi^*\vec{\nabla}\psi \;-\; \psi\vec{\nabla}\psi^*\,] \;\;.$$

With this definition we can write down a *continuity equation* analogously to the continuity equation in electrodynamics:

Theorem 2.1 (Continuity equation) $\quad \frac{\partial}{\partial t}\,\rho(t,\vec{x}) \;+\; \vec{\nabla}\,\vec{j}(t,\vec{x}) \;=\; 0$

Theorem 2.1 implies the *conservation of probability* for all times

$$\int_{-\infty}^{\infty} d^3x\,|\psi(t,\vec{x})|^2 \;=\; 1 \qquad \forall\, t \geq 0\,, \tag{2.18}$$

analogously to the charge conservation. Thus the continuity equation, Theorem 2.1, means that a change of the probability in a volume V is balanced by a probability flux leaving V. So the probability and current densities behave like actual densities.

Proof: To prove the conservation of probability (2.18) we assume that ψ is normalized to 1 at $t = 0$ and that the probability density is only nonzero in a finite region $V \in \mathbb{R}^3$. Performing the derivative of ρ with respect to time and using the continuity equation, Theorem 2.1, we get

$$\frac{\partial}{\partial t} \int\limits_V d^3x\, \rho(t,\vec{x}) \;=\; -\int\limits_V d^3x\, \vec{\nabla}\, \vec{j}(t,\vec{x}) \;\overset{Gauß}{=}\; \int\limits_{\partial V} d\vec{f}\, \vec{j}(t,\vec{x})\;. \tag{2.19}$$

We have used the Theorem of Gauß to convert the integral over a 3-dimensional space V into an integral over its (2-dimensional) boundary ∂V which, for convenience, we can assume to be a sphere S_2 with radius R. By requiring the wave function to be square integrable it has to decrease stronger than $\frac{1}{R}$ for $R \to \infty$. Therefore the probability current has to fall off like $\frac{1}{R^3}$ (since the nabla operator is proportional[3] to $1/R$: $\vec{\nabla} \propto \frac{1}{R}$).

If we consider the last integral of Eq. (2.19) in the limit $R \to \infty$, using spherical coordinates, we find it to be proportional to

$$\propto \int dR\, R^2\, \frac{1}{R^3} \;\to\; 0 \qquad \text{for} \quad R \to \infty\,. \tag{2.20}$$

So we can conclude

$$\Rightarrow \quad \int\limits_{-\infty}^{\infty} d^3x\, \rho(t,\vec{x}) \;=\; \text{const.} \;=\; 1 \qquad \text{q.e.d.} \tag{2.21}$$

Remark: The probability current $\vec{j}$ can be expressed by the *momentum operator* $\vec{P} = -i\hbar\vec{\nabla}$ by noting that

$$\begin{aligned} \vec{j}(t,\vec{x}) \;&=\; \frac{\hbar}{2mi}\,[\,\psi^*\vec{\nabla}\psi \;-\; \psi\vec{\nabla}\psi^*\,] \;= \\ &=\; \frac{1}{2m}[\,\psi^*(-i\hbar\vec{\nabla})\psi \;+\; (\psi^*(-i\hbar\vec{\nabla})\psi)^*\,] \;= \\ &=\; \frac{1}{m}\mathrm{Re}(\psi^*(-i\hbar\vec{\nabla})\psi) \;=\; \frac{1}{m}\mathrm{Re}(\psi^*\vec{P}\psi)\,. \end{aligned} \tag{2.22}$$

As an example we calculate the probability current of a plane wave

$$\vec{j}(t,\vec{x}) \;=\; \frac{1}{m}\mathrm{Re}\big(e^{-i(\vec{k}\vec{x}-\omega t)}(-i\hbar\vec{\nabla})e^{i(\vec{k}\vec{x}-\omega t)}\big) \;=\; \frac{1}{m}\mathrm{Re}\big(e^{-i(\vec{k}\vec{x}-\omega t)}\,\underbrace{\hbar\vec{k}}_{\vec{p}}\,e^{i(\vec{k}\vec{x}-\omega t)}\big) \;=\; \frac{\vec{p}}{m} \;=\; \vec{v} \tag{2.23}$$

and see that probability "flows" along the direction of the particle's velocity.

[3] Of course since this is an operator, this has to be understood as acting on a wave function.

2.3 Observables

In quantum mechanics there are two important concepts, which we use to describe physical objects:

1. **State of a system,** which is described by the wave function $\psi(t, \vec{x})$.

2. **Observables,** which are physical quantities we want to measure, like e.g. position, momentum, energy. These observables are represented by hermitian operators acting on the wave function.

The rules to combine these concepts are provided by quantum mechanics. We now introduce some mathematical background which we will need to set up these rules.

2.3.1 Operators

Definition 2.3 *A is called a **linear operator**, if for $A\,\psi_1(x) = \phi_1(x)$ and $A\,\psi_2(x) = \phi_2(x)$, where ψ_1, ψ_2, ϕ_1, $\phi_2 \in L_2$, follows that*

$$A(c_1\psi_1 + c_2\psi_2) = c_1\phi_1 + c_2\phi_2 \quad c_1, c_2 \in \mathbb{C}\,.$$

Remark: Linear operators, such as e.g. $\vec{\nabla}$, Δ, $\frac{\partial}{\partial t}$, $V(x)$, obey the law of distributivity (with respect to addition and multiplication in the space of linear operators) in the sense that

$$\begin{aligned} (A + B)\,\psi &= A\,\psi + B\,\psi \\ A\,B\,\psi &= A\,(B\,\psi) \end{aligned} \tag{2.24}$$

Furthermore the space of linear operators is equipped with an absorbing element (or zero operator) $\hat{0}$ and a neutral element (or unit element, or identity) $\mathbb{1}$, satisfying

$$\mathbb{1}\,\psi = \psi \quad \text{and} \quad \hat{0}\,\psi = 0 \quad \forall\,\psi \tag{2.25}$$

and which commute with every operator

$$\mathbb{1}A = A\,\mathbb{1} \quad \text{and} \quad \hat{0}A = A\,\hat{0} \quad \forall\,A\,. \tag{2.26}$$

The commutativity property, however, does not hold generally for arbitrary operators A and B

$$A\,B \neq B\,A\,. \tag{2.27}$$

2.3.2 Scalar Product

We will now introduce the notion of the *scalar product* used in quantum mechanics. This will be done in the so called "Dirac notation" of "bra's" and "ket's" which will be thoroughly investigated in Chapter 3.

Definition 2.4 *We define the* ***scalar product*** *of two wave functions ψ and ϕ by*

$$\langle \psi \,|\phi\rangle \;:=\; \int_{-\infty}^{\infty} d^3x\, \psi^*(\vec{x})\phi(\vec{x})$$

Remark: The scalar product is formally written as the product[4] of "bra" $\langle\,.\,|$ with "ket" $|\,.\,\rangle$. Other notations of this scalar product include $(\psi\,,\,\phi)$ and $\langle\psi\,,\,\phi\rangle$. If the wave function depends on discrete variables, e.g. spin orientation, instead of continous ones, like e.g. position, the scalar product from Definition 2.4 reduces to

$$\langle \psi \,|\phi\rangle \;=\; \sum_k \psi_k^*\,\phi_k \;. \tag{2.28}$$

Properties of the scalar product:

$$\langle \phi \,|\psi\rangle^* \;=\; \langle \psi \,|\phi\rangle \tag{2.29}$$

$$\langle \phi \,|c_1\psi_1 \,+\, c_2\psi_2\rangle \;=\; c_1\,\langle \phi \,|\psi_1\rangle \,+\, c_2\,\langle \phi \,|\psi_2\rangle \quad \text{linear in "ket"} \tag{2.30}$$

$$\langle c_1\phi_1 \,+\, c_2\phi_2 \,|\psi\rangle \;=\; c_1^*\,\langle \phi_1 \,|\psi\rangle \,+\, c_2^*\,\langle \phi_2 \,|\psi\rangle \quad \text{antilinear in "bra"} \tag{2.31}$$

$$\langle \psi \,|\psi\rangle \;>\; 0 \quad \forall\,\psi \,\neq\, 0, \qquad \langle \psi \,|\psi\rangle \;=\; 0 \quad \Leftrightarrow \quad \psi \,\equiv\, 0 \quad \text{positive definite} \tag{2.32}$$

Operators in the scalar product: [5]

Suppose A is an operator satisfying $A\,\psi \,=\, \phi$, where $\psi,\, \phi \,\in\, L_2$, then

$$\langle \psi \,|A\,\phi\rangle \;=\; \int d^3x\, \psi^*(\vec{x}) A\,\phi(\vec{x}) \;. \tag{2.33}$$

[4] Strictly speaking, this is only a product in the sense that one object acts on the other (from the left side).

[5] We will omit the limits of the integration in the scalar product from now on and implicitly assume them to be $\pm\infty$ unless stated otherwise.

Definition 2.5 *$A^\dagger$ is called the **adjoint operator** to A, if $\forall\ \psi, \phi \in L_2$*

$$\left\langle A^\dagger \psi \,|\phi\right\rangle \;=\; \langle \psi \,|A\,\phi\rangle \;.$$

That means more explicitly

$$\int d^3x\, A^\dagger\, \psi^*(\vec{x})\phi(\vec{x}) \;=\; \int d^3x\, \psi^*(\vec{x}) A\,\phi(\vec{x})\,. \tag{2.34}$$

In matrix notation we can write the the adjoint[6] matrix as the complex conjugation of the transposed matrix or vice versa, i.e. $A^\dagger = (A^{\mathrm{T}})^* = (A^*)^{\mathrm{T}}$.

Here the operator in the scalar product is assumed to act to the right side[7], justifying the notation

$$\langle\psi|\, A\,|\phi\rangle \;=\; \langle \psi \,|A\,\phi\rangle \;. \tag{2.35}$$

Definition 2.6 *An Operator A is called **hermitian**, if*

$$A^\dagger \;=\; A$$

and the domains satisfy $D(A^\dagger) \supset D(A)$

If $D(A^\dagger) = D(A)$, then A is called self-adjoint.

Since the difference between hermitian and self-adjoint operators only plays a role for unbounded operators, we will neglect it here and use the terms synonymously.

Examples:

- **Position operator** X $\qquad X\psi(x) \;=\; x\,\psi(x)$

  defined for functions ψ, satisfying:

  $$\langle X\psi \,|X\psi\rangle \;=\; \int dx\, x^2\, |\psi(x)|^2 \;<\; \infty\;. \tag{2.36}$$

  The generalization to 3 dimensions[8] is straightforward by labeling the above operator X as X_{i}, the i-th compononent of a vector operator $\vec{X}$. In this case we also require the integral in Eq. 2.36 to be finite when carried out over d^3x.

  The position operator X is a **hermitian** operator.

[6] The adjoint operator is also called the hermitian conjugate (mainly by physicists).

[7] This is not always the case but operators acting otherwise are often noted with arrows indicating their direction of action, e.g. $\overleftarrow{D}, \overleftrightarrow{D}$

[8] In the following we will mostly ignore the generalizations to 3 dimensions, since these can (mostly) be done by simple replacements, e.g. $x \to \vec{x}$, $dx \to d^3x$, at the most accompanied by constant factors due to Fourier transformations, but won't help us to gain any more insight in the physical or mathematical processes involved.

- **Momentum operator** P $\qquad P\psi(x) \;=\; -i\hbar\nabla\,\psi(x)$

  defined for functions ψ, satisfying:

$$\langle P\psi\,|P\psi\rangle \;=\; \hbar^2\int dx\,|\nabla\psi(x)|^2 \;<\; \infty\,. \tag{2.37}$$

  For example, for a plane wave $\psi(x) = e^{ixp/\hbar}$, we get[9] $\quad P\psi(x) = p\,\psi(x)$.

  The momentum operator also is **hermitian**: $P^\dagger = P$.

- **Hamiltonian** H $\qquad H\psi(x) \;=\; \left(-\frac{\hbar^2}{2m}\Delta \;+\; V(x)\right)\,\psi(x) \;=\; E\psi(x)$

  which is defined for $\psi's$ such that

$$\langle H\psi\,|H\psi\rangle \;=\; E^2\int dx\,|\psi(x)|^2 \;<\; \infty\,. \tag{2.38}$$

2.4 Expectation Values

Having now explained some basic concepts in quantum mechanics, wave functions, scalar products and observables, we now need to discuss the rules that quantum mechanics provides to make physical predictions. Let's first remember the concepts from Section 2.3 and make them a little more precise:

Definition 2.7 *The **state** of a quantum mechanical system is represented by a vector $|\psi\rangle$ (ket) in a complex vectorspace, called Hilbertspace, equipped with a scalar product.*

Definition 2.8 ***Observables** in quantum mechanics are represented by hermitian operators acting on the state vectors in Hilbertspace.*

2.4.1 Expectation Values of Operators

We now want to find a way to relate these theoretical concepts with experimental outcomes, i.e., measurements. Since we already assume quantum mechanics to be of a statistical character (remember Born's probability interpretation, Prop. 1.7.1), let's take a brief look at some concepts of classical statistics.

If we want to calculate the average of a set of values $\{x_i\}$, we do so by calculating the *arithmetic mean*

$$\overline{x} \;=\; \frac{1}{n}\sum_{i=1}^{n} x_i\,. \tag{2.39}$$

[9] remember $p/\hbar = k$ (Eq. 1.22)

If the possible values are not equally probable, we use the *weighted arithmetic mean*

$$\overline{x} \;=\; \frac{\sum_{i=1}^{n} w_i\, x_i}{\sum_{i=1}^{n} w_i}\,. \tag{2.40}$$

For a (Riemann-integrable) function $f(x)$ we can generalize the arithmetic mean to

$$\overline{f} \;=\; \frac{1}{b-a}\int_a^b dx\, f(x)\,. \tag{2.41}$$

Analogously to Eq. (2.40) we introduce a weight-function $w(x)$, which we can interpret as probability distribution, to get

$$\overline{f} \;=\; \frac{\int_a^b dx\, w(x)\, f(x)}{\int_a^b dx\, w(x)}\,. \tag{2.42}$$

Returning now to quantum mechanics, we notice the resemblance of Eq. (2.42) to the operator in the scalar product (Eq. 2.33), when interpreting $\psi^*\psi$ as a probability distribution. Thus we can write the weighted mean value of an operator A as

$$\langle A \rangle \;=\; \frac{\langle\psi|\, A\,|\psi\rangle}{\langle\psi\,|\psi\rangle}\,. \tag{2.43}$$

Since we require our wave function to be normalized to 1 (Eq. 2.9) we define:

Definition 2.9 *The **expectation value** of an observable A in the state $|\psi\rangle$ is given by*

$$\langle A \rangle_\psi \;=\; \langle\psi|\, A\,|\psi\rangle\,.$$

The expectation value $\langle A \rangle_\psi$ gives us the outcome of a series of measurements of the observable A of a physical system prepared in the state ψ. It thus has a physical meaning with respect to predicting measurement outcomes for an ensemble of identically prepared objects, even if the individual results are at random.

Properties of the expectation value:

$$\text{I)} \quad \langle \mathbb{1} \rangle = \langle \psi \, | \psi \rangle = 1 \tag{2.44}$$

$$\text{II)} \quad \begin{array}{ll} \langle A \rangle \in \mathbb{R} & \text{if } A \text{ is hermitian} \quad A = A^\dagger \\ \langle A \rangle \in i \cdot \mathbb{R} & \text{if } A \text{ is anti-hermitian} \quad A = -A^\dagger \end{array} \tag{2.45}$$

$$\text{III)} \quad \langle A \rangle \geq 0 \qquad \text{if } A \text{ is a positive operator} \quad A \geq 0 \tag{2.46}$$

$$\text{IV)} \quad \langle A \rangle \text{ is linear} \qquad \langle \alpha A + \beta B \rangle = \alpha \langle A \rangle + \beta \langle B \rangle \quad \alpha, \beta \in \mathbb{C}, \quad A, B \text{ linear operators} \tag{2.47}$$

Examples:

- **Expectation value of a potential $V(x)$**

$$\langle V(x) \rangle = \langle \psi | V(x) | \psi \rangle = \int dx \, V(x) \, |\psi(x)|^2 \tag{2.48}$$

  In accordance with our consideration of classical statistics this is exactly the classical expectation for a potential controlled by a distribution $|\psi(x)|^2$.

- **Expectation value of the position operator X**

$$\langle X \rangle = \langle \psi | X | \psi \rangle = \int dx \, x \, |\psi(x)|^2 \tag{2.49}$$

  For the postition operator we again get the classical result for the variable x, distributed by the probability density $|\psi(x)|^2$.

- **Expectation value of the momentum operator P**

$$\langle P \rangle = \langle \psi | P | \psi \rangle = -i\hbar \int dx \, \psi(x)^* \nabla \psi(x) = \int_{-\infty}^{\infty} dp \, p \, |\tilde{\psi}(p)|^2 \tag{2.50}$$

  $|\tilde{\psi}(p)|^2$ takes over the role of the probability density for the momentum-variable.

The function $\tilde{\psi}(p)$ is the Fourier-transform[10] of the wave function $\psi(x)$

$$\tilde{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int dx \, \exp\left(-\frac{i}{\hbar} p x\right) \psi(x) \, . \tag{2.51}$$

[10]The change of variables, $k = p/\hbar$, also requires the inclusion of $\hbar$ in the factor $1/\sqrt{2\pi}$ that normally occurs in the Fourier transformation.

Proof: To prove the last step of Eq. (2.50) we form the inverse transformation to Eq. (2.51)

$$\psi(x) \;=\; \frac{1}{\sqrt{2\pi\hbar}} \int dp \; \exp\,(\frac{i}{\hbar} px) \tilde{\psi}(p) \tag{2.52}$$

and insert it into the expectation value of P, Eq. (2.50),

$$\begin{aligned} \langle\, P \,\rangle \;&=\; \frac{1}{2\pi\hbar} \int dx \int dp \int dp' \; \exp\,(-\frac{i}{\hbar} p'x) \tilde{\psi}^*(p') (-i\hbar\nabla) \; \exp\,(\frac{i}{\hbar} px)\, \tilde{\psi}(p) \;= \\ &=\; \frac{1}{2\pi\hbar} \int dx \int dp \int dp' \; \exp\,(-\frac{i}{\hbar} p'x) \tilde{\psi}^*(p')\, p \;\; \exp\,(\frac{i}{\hbar} px) \tilde{\psi}(p) \;= \\ &=\; \frac{1}{2\pi\hbar} \int dp \int dp' \; \int dx \; p \; \exp\,(\frac{i}{\hbar}(p-p')x)\, \tilde{\psi}^*(p')\, \tilde{\psi}(p)\,. \end{aligned} \tag{2.53}$$

Now we use the Dirac delta distribution

$$\delta(p-p') \;=\; \frac{1}{2\pi\hbar} \int dx \; \exp\,(\frac{i}{\hbar}(p-p')x)\,, \tag{2.54}$$

which is defined[11] by its action in an integration

$$\int_{-\infty}^{\infty} dx'\, \delta(x-x')\, f(x') \;=\; f(x)\,. \tag{2.55}$$

With help of formulas (2.54) and (2.55) we can rewrite Eq. (2.53) as

$$\text{Eq. (2.53)} \;=\; \int dp \int dp' \;\; p\, \delta(p-p') \;\, \tilde{\psi}^*(p')\, \tilde{\psi}(p) \;=\; \int dp \; p\, |\tilde{\psi}(p)|^2 \qquad \text{q.e.d.} \tag{2.56}$$

2.4.2 Uncertainty of Observables

As we now know how to compute the quantum mechanical predictions for measurement outcomes, we want to go a step further by calculating how trustworthy our predictions are. That means, how much possible measurement outcomes will vary or deviate, leading to a variance, or a mean-square deviation, or an uncertainty. To do this we again investigate the methods of classical statistics.

Performing a series of measurements with outcomes $\{x_{\rm i}\}$ we already know from Eq. (2.39) and Eq. (2.40) how to calculate the mean values. If we started from there by calculating the deviations of the individual values from their mean value, then some of the deviations might cancel each other in the sum since these deviations could have either sign. Therefore it's better to compute the arithmetic mean of the squared deviations, the *variance*

$$\sigma^2 \;=\; \frac{1}{n} \sum_{i=1}^{n} (x_{\rm i} - \overline{x})^2\,. \tag{2.57}$$

[11] For a more rigorous definition we must refer the interested reader to a standard lecture, see e.g. Ref. [13], and/or textbook on functional analysis.

We then take its square-root, the *standard deviation*, which gives us a measure for the width of the distribution, i.e., how good the mean value approximates the individual results, see Fig. 2.2,

$$\sigma \;=\; \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_{\rm i}-\overline{x})^2}\,. \tag{2.58}$$

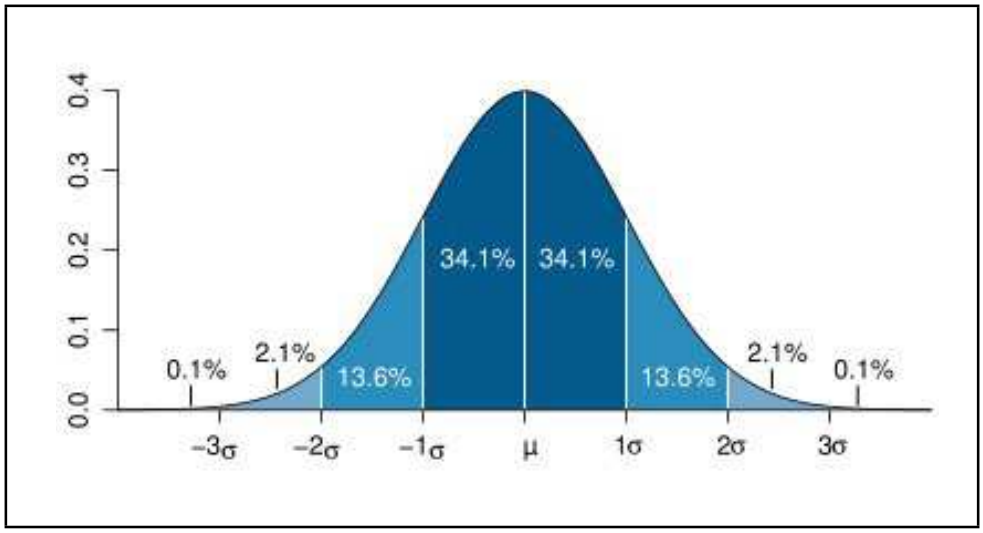

Figure 2.2: Standard deviation: In this normal (or "Gaussian") distribution we can see how the standard deviation σ quantifies the probability of finding the next result in σ-intervals around the mean value; figure from http://en.wikipedia.org/wiki/Image:Standard_deviation_diagram.svg

To convey this concepts to quantum mechanics we start by defining a deviation operator $\overline{A}$ associated with our observable A

$$\overline{A} \;:=\; A - \langle\, A\,\rangle\;. \tag{2.59}$$

To compute the variance we calculate the expectation value of the squared deviation operator

$$\begin{aligned}\left\langle\, \overline{A}^{\,2}\,\right\rangle \quad &= \quad \left\langle\, A^2 - 2A\,\langle\, A\,\rangle + \langle\, A\,\rangle^2\,\right\rangle \quad = \\ &= \langle\, A^2\,\rangle - 2\,\langle\, A\,\rangle\,\langle\, A\,\rangle + \langle\, A\,\rangle^2 \quad = \\ &= \langle\, A^2\,\rangle - \langle\, A\,\rangle^2 =: (\Delta A)^2\,. \end{aligned} \tag{2.60}$$

Finally, we take the square root and define the variance or uncertainty.

Definition 2.10 *The **uncertainty** of an observable A in the state $|\psi\rangle$ is given by*

$$\Delta A \;=\; \sqrt{\langle\, A^2 \,\rangle_\psi \;-\; \langle\, A \,\rangle_\psi^2}\;\;.$$

The uncertainty of an observable represents a variation or fluctuation of possible measurement outcomes and it depends on the state $|\psi\rangle$ of the system. Although we followed here ideas of classical statistics we must stress that the uncertainty of an operator is not related to any technical imperfections of the measurement process. It is an important, genuine quantum feature !

The uncertainty can even vanish (much unlike technical imperfections) for certain states, which we will formulate by the following theorem.

Theorem 2.2 *The uncertainty of an observable A vanishes if, and only if, the state $|\psi\rangle$ of the system is an eigenvector of the operator A.*

$$\Delta A \;=\; 0 \qquad \Leftrightarrow \qquad A\,|\psi\rangle \;=\; a\,|\psi\rangle$$

The value $a \in \mathbb{R}$ is called the *eigenvalue*[12] of A, corresponding to the eigenvector $|\psi\rangle$.

Proof:

$$\begin{aligned}
\langle\, A \,\rangle_\psi \;=\;& \langle\psi|\; A\;|\psi\rangle \;=\; \langle\psi|\; a\;|\psi\rangle \;\overset{a\in\mathbb{R}}{=}\; a\,\langle\psi\,|\psi\rangle \;=\; a \qquad \Rightarrow\quad \langle\, A \,\rangle^2 \;=\; a^2 \\
\langle\, A^2 \,\rangle_\psi \;=\;& \langle\psi|\; A\,A\;|\psi\rangle \;=\; \langle\psi|\; a^2\;|\psi\rangle \;\overset{a^2\in\mathbb{R}}{=}\; a^2\,\langle\psi\,|\psi\rangle \;=\; a^2 \qquad \Rightarrow\quad \langle\, A^2 \,\rangle \;=\; a^2 \\
\Rightarrow\quad & \Delta A \;=\; \sqrt{\langle\, A^2 \,\rangle_\psi \;-\; \langle\, A \,\rangle_\psi^2} \;=\; \sqrt{a^2 \;-\; a^2} \;=\; 0 \qquad \text{q.e.d.}
\end{aligned}$$

2.5 Commutator of Operators

Up to now we have only considered individual operators or at the most products of the same operator, which didn't cause a problem. However, if we multiply different operators, we face an interesting consequence. Generally, those products are not commutative, which means that the order of application of the operators does matter, i.e.:

$$A\,B \;\neq\; B\,A\,. \tag{2.61}$$

[12]For general operators the eigenvalues would be complex numbers, but for hermitian operators, i.e. observables, the eigenvalues are real.

Take, for example, position and momentum operator X and P

$$X\,\psi(x) \;=\; x\,\psi(x) \qquad P\,\psi(x) \;=\; -i\hbar\nabla\,\psi(x)\,, \tag{2.62}$$

and consider the action of a combination of these operators on a wave function

$$P\,X\,\psi(x) \;=\; -i\hbar\nabla\,(x\,\psi(x)) \;=\; -i\hbar\,\psi(x) - i\hbar\,x\,\nabla\,\psi(x) \;=\; -i\hbar\,\psi(x) + X\,P\,\psi(x)\,, \tag{2.63}$$

then we can write formally

$$X\,P \;=\; P\,X \;+\; i\hbar\,. \tag{2.64}$$

To further formalize relations between operators we introduce the so-called *commutator* of operators.

Definition 2.11 *The* ***commutator*** $[\,.\,,\,.\,]$ *of two operators* A *and* B *is given by*

$$[\,A\,,\,B\,] \;=\; A\,B \;-\; B\,A$$

Thus we rewrite Eq. (2.64) as commutator of X and P

$$[\,X\,,\,P\,] \;=\; i\hbar\,, \tag{2.65}$$

which is part of an important theorem.

Theorem 2.3 (Canonical commutation relations)
The components of the 3*-dimensional position and momentum operator are related by*

$$[\,X_{\mathrm{i}}\,,\,P_{\mathrm{j}}\,] \;=\; i\hbar\,\delta_{\mathrm{ij}}\;, \qquad [\,X_{\mathrm{i}}\,,\,X_{\mathrm{j}}\,] \;=\; [\,P_{\mathrm{i}}\,,\,P_{\mathrm{j}}\,] \;=\; 0$$

Properties of the commutator:

$$\text{I)} \qquad [A\,,\,B] = -\,[B\,,\,A] \qquad \Rightarrow [A\,,\,A] = 0 \tag{2.66}$$

$$\text{II)} \qquad [A\,,\,B] \quad \text{is linear in } A \text{ and } B \tag{2.67}$$

$$\text{III)} \qquad [A\,,\,B]^\dagger = \left[A^\dagger\,,\,B^\dagger\right] \tag{2.68}$$

$$\text{IV)} \qquad [A\,,\,BC] = B\,[A\,,\,C] + [A\,,\,B]\,C \tag{2.69}$$

$$\text{V)} \quad [A\,,[B\,,C]] + [B\,,[C\,,A]] + [C\,,[A\,,B]] = 0 \quad \text{Jacobi-identity} \tag{2.70}$$

$$\text{VI)} \quad e^A\,B\,e^{-A} = B + [A\,,\,B] + \tfrac{1}{2!}[A\,,[A\,,\,B]] + \cdots \quad \text{Baker-Campbell-Hausdorff formula} \tag{2.71}$$
$$\text{where} \quad e^A = \textstyle\sum \frac{1}{n!} A^n$$

$$\text{VII)} \quad e^A\,e^B = e^B\,e^A\,e^{[A\,,B]} \quad \text{and} \quad e^{A+B} = e^A\,e^B\,e^{-[A\,,B]/2} \tag{2.72}$$
$$\text{if} \quad [[A\,,\,B]\,,\,A] = [[A\,,\,B]\,,\,B] = 0$$

2.6 Uncertainty Principle

As we have learned in Section 2.4.2 the uncertainty of an observable is the quantum mechanical analogue of the classical standard deviation in the results of repeated measurements on identically prepared objects.

2.6.1 Uncertainty Relation for Observables

The non-commutativity of two observables has profound consequences, it is deeply related to the uncertainty of these observables. Let's recall the deviation operator (2.59) and the corresponding variance (2.60) then we can formulate the following theorem.

Theorem 2.4 (Uncertainty relation)
Let A and B be two observables, then the following inequality, the ***uncertainty relation****, is valid for all states*

$$\Delta A\ \Delta B \geq \tfrac{1}{2}|\,\langle [A\,,\,B]\rangle\,|$$

Whenever the commutator of two observables is nonvanishing, there is an uncertainty of these observables.

Proof: Let's start by defining the following non-hermitian operator Z

$$Z := \frac{\overline{A}}{\Delta A} + i\,\frac{\overline{B}}{\Delta B}\,, \tag{2.73}$$

where $\overline{A}$ and $\overline{B}$ are defined in Eq. (2.59). We consider the scalar product

$$\langle Z\psi\,|Z\psi\rangle \;=\; \langle\psi|\,Z^{\dagger}Z\,|\psi\rangle \;\geq\; 0\,, \tag{2.74}$$

which is definitely positive, Eq. (2.32), and use the definition of the adjoint operator, Definition 2.5. Inserting operator Z, Eq. (2.73), into the scalar product and noting that $Z^{\dagger} = (Z^{\mathrm{T}})^{*}$ we get

$$\langle\psi|\left(\frac{\overline{A}}{\Delta A} - i\,\frac{\overline{B}}{\Delta B}\right)\left(\frac{\overline{A}}{\Delta A} + i\,\frac{\overline{B}}{\Delta B}\right)|\psi\rangle \;\geq\; 0\,. \tag{2.75}$$

Multiplying the brackets and recalling that operators generally do not commute, gives

$$\langle\psi|\left(\frac{\overline{A}^{\,2}}{(\Delta A)^2} + i\,\frac{\overline{A}\,\overline{B} - \overline{B}\,\overline{A}}{\Delta A\Delta B} + \frac{\overline{B}^{\,2}}{(\Delta B)^2}\right)|\psi\rangle \;\geq\; 0\,. \tag{2.76}$$

Since the expectation values of $\overline{A}^{\,2}$ and $\overline{B}^{\,2}$ are just the squares of the corresponding variances, Eq. (2.60), the first and third term (each separately) give just 1. Using the commutator we may write

$$2 \;\geq\; -i\,\frac{\langle\psi|\left[\,\overline{A}\,,\,\overline{B}\,\right]|\psi\rangle}{\Delta A\,\Delta B} \;=\; -i\,\frac{\langle\psi|\left[\,A - \langle\,A\,\rangle\,,\,B - \langle\,B\,\rangle\,\right]|\psi\rangle}{\Delta A\,\Delta B} \;=\; -i\,\frac{\langle\psi|\left[\,A\,,\,B\,\right]|\psi\rangle}{\Delta A\,\Delta B}\,. \tag{2.77}$$

Rewriting Eq. (2.77) we finally obtain

$$\Delta A\,\Delta B \;\geq\; \frac{1}{2}\,|\,\langle[\,A\,,\,B\,]\rangle\,| \qquad \text{q.e.d.} \tag{2.78}$$

Note: Inequality (2.77) is certainly valid since the factor $(-i)$ is compensated by the pure imaginary scalar product $\langle\psi|\,[\,A\,,\,B\,]\,|\psi\rangle$, Eq. (2.45), due to the anti-hermiticity of the commutator of two hermitian operators

$$[\,A\,,\,B\,]^{\dagger} \;=\; \left[\,B^{\dagger}\,,\,A^{\dagger}\,\right] \;=\; [\,B\,,\,A\,] \;=\; -\,[\,A\,,\,B\,]\,. \tag{2.79}$$

Example: Position and momentum

Choosing in Theorem 2.3 as observables position and momentum $A = X$ and $B = P$ and recalling the canonical commutation relation (2.65) we recover the uncertainty relation we proposed in Section 1.6

$$\Delta X\,\Delta P \;\geq\; \frac{\hbar}{2}\,. \tag{2.80}$$

This inequality holds for all states, but it is saturated (it becomes an equality) for Gaussian wave packets (see Section 2.8) and, in particular, for the Gaussian ground state of the harmonic oscillator (see Section 4.7).

2.6.2 Energy–Time Uncertainty

In order to derive the energy–time uncertainty relation, we need to take a closer look on how time is treated within quantum mechanics. We know that in special relativity time and space are treated on equal footing by introducing the notion of so-called 4-vectors, $x^\mu = (ct, \vec{x})^T$, $p^\mu = (\frac{E}{c}, \vec{p})^T$, which include both time- and space-coordinates.

In nonrelativistic quantum mechanics, however, time t and space x have a different significance. Whereas x and p are the eigenvalues of the observables X and P respectively – physical quantities, for this reason – the time t is only an independent variable, a parameter. We are measuring space x and momentum p at a certain time t. Thus there does not exist such a thing as a "time operator" [13], whose eigenvalues represent possible time measurement results.

We can, however, analyze the change of a physical system within a short interval of time. Let's denote Δt as the time variation that is necessary for the system to undergo a substantial change.

As a measure for the change of the system we calculate the derivative with respect to time of the expectation value of some observable $A(t, x, p)$

$$\frac{d}{dt}\langle A \rangle = \frac{d}{dt}\langle \psi | A | \psi \rangle = \langle \dot{\psi} | A | \psi \rangle + \langle \psi | \dot{A} | \psi \rangle + \langle \psi | A | \dot{\psi} \rangle , \tag{2.81}$$

where we have used the notation $\dot{\psi} = \frac{\partial}{\partial t}\psi$. Using the Schrödinger equation (Eq. 2.14) and its complex conjugate (Eq. 2.15) we get

$$\frac{d}{dt}\langle A \rangle = \frac{i}{\hbar}\langle \psi | HA - AH | \psi \rangle + \langle \psi | \frac{\partial}{\partial t}A | \psi \rangle . \tag{2.82}$$

Theorem 2.5 (Time evolution of expectation value)
The time evolution of the expectation value is given by
- *the commutator of the observable with the Hamiltonian*
- *the time evolution of the observable*

$$\frac{d}{dt}\langle A \rangle = \frac{i}{\hbar}\langle [H, A] \rangle + \langle \frac{\partial}{\partial t}A \rangle$$

Remark I: Classical Analogy
There is a classical analogy to Theorem 2.5. In classical (Hamiltonian) mechanics observables are represented by functions $f(p_i, q_i, t)$ on phase space, where p_i, q_i are the canonical coordinates. Such functions obey the following relation:

$$\frac{d}{dt}f(p_i, q_i, t) = \{ H, f \} + \frac{\partial}{\partial t}f(p_i, q_i, t) , \tag{2.83}$$

[13] There exists, however, the notion of a time-translation operator, which we will encounter later on.

where H is Hamilton's principal function and $\{\,.\,,\,.\,\}$ denotes the Poisson-bracket

$$\{\,f\,,\,g\,\} \;=\; \sum_{i=1}^{N}\left[\frac{\partial f}{\partial q_i}\frac{\partial g}{\partial p_i} \;-\; \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial q_i}\right]. \tag{2.84}$$

The transition from the Poisson bracket of classical mechanics to the commutator of quantum mechanics

$$\{\,.\,,\,.\,\} \qquad \Rightarrow \qquad -\frac{i}{\hbar}\,[\,.\,,\,.\,] \tag{2.85}$$

is quite generally valid and is called Dirac's rule. Compare, e.g., the canonical commutation relations (Theorem 2.3) or the Liouville equation (see theorem 8.2) with the corresponding classical relations.

Remark II: Conserved Observables
We obtain a special case of Theorem 2.5 by considering observables that do not explicitly depend on time. Then the partial derivative of the operator A with respect to time vanishes and the time evolution of the expectation value is determined just by the commutator of A with the Hamiltonian H, i.e.

$$\frac{d}{dt}\,\langle\,A\,\rangle \;=\; \frac{i}{\hbar}\,\langle\,[\,H\,,\,A\,]\,\rangle\,. \tag{2.86}$$

If the commutator of observable A with Hamiltonian H vanishes its expectation value remains constant in time, or, we may say, the observable is conserved,

$$[\,H\,,\,A\,] \;=\; 0 \qquad \Rightarrow \qquad \frac{d}{dt}\,\langle\,A\,\rangle \;=\; 0 \qquad \Rightarrow \qquad \langle\,A\,\rangle \;=\; \text{const.} \tag{2.87}$$

Consider, for example, a free particle and its momentum P. The Hamiltonian for the free motion is given by

$$H \;=\; \frac{-\hbar^2}{2m}\Delta \;=\; \frac{P^2}{2m}\,, \tag{2.88}$$

which, according to Theorem 2.3, commutes with the momentum operator P. Thus, for free particles, momentum is a conserved quantity.

Let's now return to the general uncertainty relation for observables (Theorem 2.4) and assume the observable A to be explicitly independent of time[14]. Choosing $B = H$ we get

$$\Delta A\;\Delta H \;\geq\; \frac{1}{2}|\,\langle[\,A\,,\,H\,]\rangle\,| \;\overset{\text{Eq. (2.86)}}{=}\; \frac{\hbar}{2}\left|\frac{d}{dt}\,\langle\,A\,\rangle\right|. \tag{2.89}$$

We also formalize our statement from the beginning, that Δt is the time variation for a substantial change of the observable A, by defining

[14]This turns out to be a reasonable assumption as all practicable observables, e.g. position, momentum, angular momentum, satisfy this condition.

Definition 2.12 *Δt is the time passing, while the expectation value of the observable changes by one unit of ΔA*

$$\Delta A \;=\; \left|\tfrac{d}{dt}\,\langle\, A\,\rangle\right|\,\Delta t\,.$$

Subsequently we identify ΔH with ΔE, the uncertainty of energy, to obtain

$$\Delta E\,\Delta t \;\geq\; \frac{\hbar}{2}\,. \tag{2.90}$$

So we find, whenever an observable changes rapidly with time ($\frac{d}{dt}\langle\, A\,\rangle$ big) Δt will be small resulting in a high energy uncertainty, and vice versa. If the system remains stable (stationary), i.e. $\frac{d}{dt}\langle\, A\,\rangle \;=\; 0$, then clearly there is no energy uncertainty at all (the system has a "sharp" energy). Later on, we again look at this statement from the perspective of eigenvalue equations (Chapter 4).

2.7 Ehrenfest Theorem and Virial Theorem

We want to present two theorems that link quantum mechanics to classical mechanics.

2.7.1 Ehrenfest Theorem

Classical Newtonian mechanics follows from quantum mechanics in the sense of Ehrenfest's theorem, which we will derive in the following. We start by considering Theorem 2.5, the theorem for the time evolution of the expectation value of an operator. As operators we choose the position and momentum whose partial time-derivatives are vanishing. Thus we are left with the calculation of the corresponding commutators with the Hamiltonian of a particle in an exterior potential $V(\vec{x})$

$$H \;=\; \frac{-\hbar^2}{2m}\Delta \,+\, V(\vec{x}) \;=\; \frac{\vec{P}^2}{2m} \,+\, V(\vec{x})\,, \tag{2.91}$$

$$[\,H\,,\,X_{\rm i}\,] \;=\; \frac{1}{2m}\left[\,P_{\rm i}^2\,,\,X_{\rm i}\,\right] \;=\; \frac{P_{\rm i}}{2m}\underbrace{[\,P_{\rm i}\,,\,X_{\rm i}\,]}_{-i\hbar} + \underbrace{[\,P_{\rm i}\,,\,X_{\rm i}\,]}_{-i\hbar}\frac{P_{\rm i}}{2m} \;=\; -i\hbar\frac{P_{\rm i}}{m}\,, \tag{2.92}$$

$$[\,H\,,\,P_{\rm i}\,] \;=\; [\,V(x_{\rm i})\,,\,-i\hbar\nabla_{\rm i}\,] \;=\; -i\hbar V(x_{\rm i})\nabla_{\rm i} \,+\, i\hbar\underbrace{\nabla_{\rm i}V(x_{\rm i})}_{(\nabla V)+V\nabla} \;=\; i\hbar\,(\nabla_{\rm i}V(x_{\rm i}))\;. \tag{2.93}$$

In Eq. (2.92) we have used property (2.69) of a commutator and the canonical commutation relations (Theorem 2.3).

We now consider Theorem 2.5 and introduce a (conservative) force $\vec{F} \;=\; -\vec{\nabla}V(\vec{x})$ to get

$$\frac{d}{dt}\langle\,\vec{X}\,\rangle \;=\; \frac{1}{m}\langle\,\vec{P}\,\rangle \tag{2.94}$$

$$\frac{d}{dt}\langle\,\vec{P}\,\rangle \;=\; -\langle\,\vec{\nabla}V\,\rangle \;=\; \langle\,\vec{F}\,\rangle\;. \tag{2.95}$$

When combining both equations, Eq. (2.94) and Eq. (2.95), we can formulate the following theorem.

Theorem 2.6 (Ehrenfest theorem)
The classical equations of motion are valid for the mean values of the operators.

$$m\frac{d^2}{dt^2}\langle \vec{X} \rangle = -\langle \vec{\nabla} V \rangle = \langle \vec{F} \rangle$$

Remark I: Planck's constant $\hbar$ does not occur in the Ehrenfest theorem, which is already a sign for the classical nature of the statement.

Remark II: For the classical equation of motion to be valid also for the mean value $\langle \vec{x} \rangle$, we have to assume that

$$\langle \vec{F}(\vec{x}) \rangle = \vec{F}(\langle \vec{x} \rangle) . \tag{2.96}$$

This condition is satisfied if the second and all higher derivatives of the force vanish, i.e. $\nabla^{\mathrm{n}}\vec{F} = 0,\ n = 2, 3, ...$; It is the case, e.g., for the free motion, the harmonic oscillator, and approximately for all slow changing forces $\vec{F}$.

2.7.2 Virial Theorem

The virial theorem is an important theorem in statistical mechanics, which relates the mean value of the kinetic energy of N particles to the one of the gradient of their potential

$$2\langle T \rangle_{\text{time average}} = \left\langle \sum_{i=1}^{N} \vec{\nabla}_{\mathrm{i}} V \cdot \vec{x}_{\mathrm{i}} \right\rangle_{\text{time average}} , \tag{2.97}$$

where $\vec{x}_{\mathrm{i}}$, ∇_{i} denote the position vector and the gradient of the i-th particle respectively. We can derive such a relation also within quantum mechanics.

We again start from Theorem 2.5 and choose as operator XP. Since the partial derivative with respect to time of XP vanishes we only have to consider the commutator with the Hamiltonian H (given by Eq. (2.91))

$$\begin{aligned} [H, XP] &\overset{Eq.\ (2.69)}{=} X[H, P] + [H, X]P = \\ \text{Eq. (2.92), (2.93)} \ \Rightarrow \quad &= X\, i\hbar\nabla V(x) - i\hbar\frac{P^2}{m} = \\ &= \frac{\hbar}{i}\left(2T - X\frac{d}{dx}V(x)\right) , \end{aligned} \tag{2.98}$$

where we denoted the kinetic energy by T and replaced the nabla operator by the total derivative. Thus we conclude that

$$\frac{d}{dt}\langle XP\rangle = 2\langle T\rangle - \langle X\,\frac{d}{dx}V(x)\rangle\,. \tag{2.99}$$

Finally we assume stationary states which satisfy[15] $\frac{d}{dt}\langle XP\rangle = 0$ and end up with the virial theorem.

Theorem 2.7 (Virial Theorem) $\quad 2\langle T\rangle = \langle X\,\frac{d}{dx}V(x)\rangle$

Example: Harmonic oscillator
For the (one dimensional) harmonic oscillator the potential energy is given by

$$V = \frac{m\omega^2x^2}{2} \quad \Rightarrow \quad \frac{d}{dx}V = m\omega^2x\,. \tag{2.100}$$

Then the virial theorem tells us that

$$2\langle T\rangle = 2\langle\,\frac{m\omega^2x^2}{2}\,\rangle \quad \Rightarrow \quad \langle T\rangle = \langle V\rangle\,. \tag{2.101}$$

2.8 Time Evolution of the Wave Packet

In this section we want to investigate how we can relate the wave functions with the moving particles they represent and what conceptual insights arise from considering the time evolution.

2.8.1 Motion of Plane Waves and Wave Packets

Plane Waves:
Let's now consider the motion associated with a plane wave (remember Eq. (2.1))

$$\psi(t,x) = e^{i(kx-\omega t)} = \exp\left(\frac{i}{\hbar}(px-Et)\right), \tag{2.102}$$

which is a solution of the free Schrödinger equation and we restrict the wave (and thus the particle) to a finite area to overcome difficulties with the normalization.

A fixed point on the wave (e.g., the maximum) corresponds to a fixed value of the argument in the exponential, i.e. $x \pm vt =$ constant. Let us calculate this velocity v,

[15] This condition can also be regarded as a form of Hamilton's principle, since the product of position and momentum has the dimension of an action, whose variation is required to vanish.

which is the *phase velocity* $\frac{\omega}{k}$, the propagation speed of the points of constant phase of the plane wave, see Fig. 2.3

$$v_{\text{phase}} := \frac{\omega}{k} = \frac{\hbar\omega}{\hbar k} = \frac{E}{p} = \frac{p^2}{2m}\frac{1}{p} = \frac{p}{2m} = \frac{1}{2}\,v_{\text{class}}\,. \tag{2.103}$$

We see that phase velocity of a plane wave travels at half the speed of the particle it should represent. Thus identifying the phase velocity with the velocity of the (classical) particle is not very satisfactory. However, the general solution of the time-dependent Schrödinger equation is a superposition of plane waves, a wave packet, and there the situation changes.

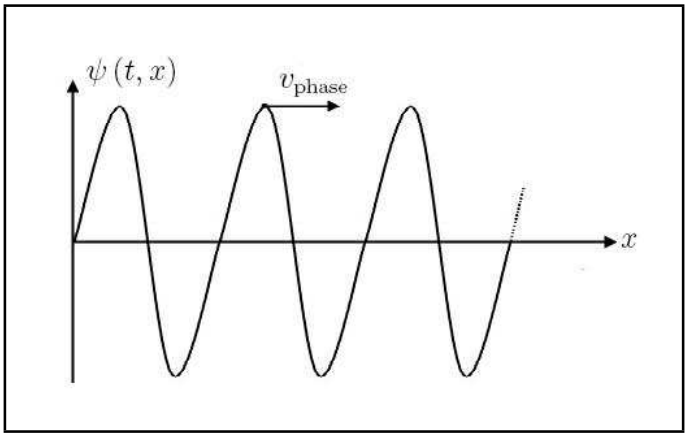

Figure 2.3: Phase velocity of a plane wave: points of constant phase, e.g., the wave crest moves with constant velocity in the x-direction.

Wave packets:
We have already encountered the wave packet in this chapter (recall Eq. (2.2)) as a solution of the Schrödinger equation

$$\psi\,(t,x) \;=\; \int\limits_{-\infty}^{\infty} \frac{dk}{\sqrt{2\pi}}\,\tilde{\psi}\,(k)\,e^{i(kx-\omega t)}\,. \tag{2.104}$$

Mathematically, it is the *Fourier transform* of a distribution $\tilde{\psi}\,(k)$ in k-space, modulated with an oscillation $\exp\,(-i\omega t)$. Thus it is just the superposition of plane waves, corresponding to different values of k, weighted with a function $\tilde{\psi}\,(k)\,/\sqrt{2\pi}$. Then the *inverse Fourier transform* at $t = 0$ has to be of the form

$$\tilde{\psi}(k) \;=\; \int\limits_{-\infty}^{\infty} \frac{dx}{\sqrt{2\pi}}\,\psi(0,x)\,e^{-ikx}\,. \tag{2.105}$$

Generally, we expect dispersion, meaning that waves of different frequencies $\omega(k)$ travel at different speeds, i.e., they have different phase velocities. The *dispersion relation*, the

relation between ω and k is given by

$$\omega(k) = \frac{\hbar k^2}{2m}\,. \tag{2.106}$$

Thus a phase velocity cannot represent the motion of the whole wave packet and we need to find another type of velocity. It is the *group velocity* v_{group}, as illustrated in Fig. 2.4.

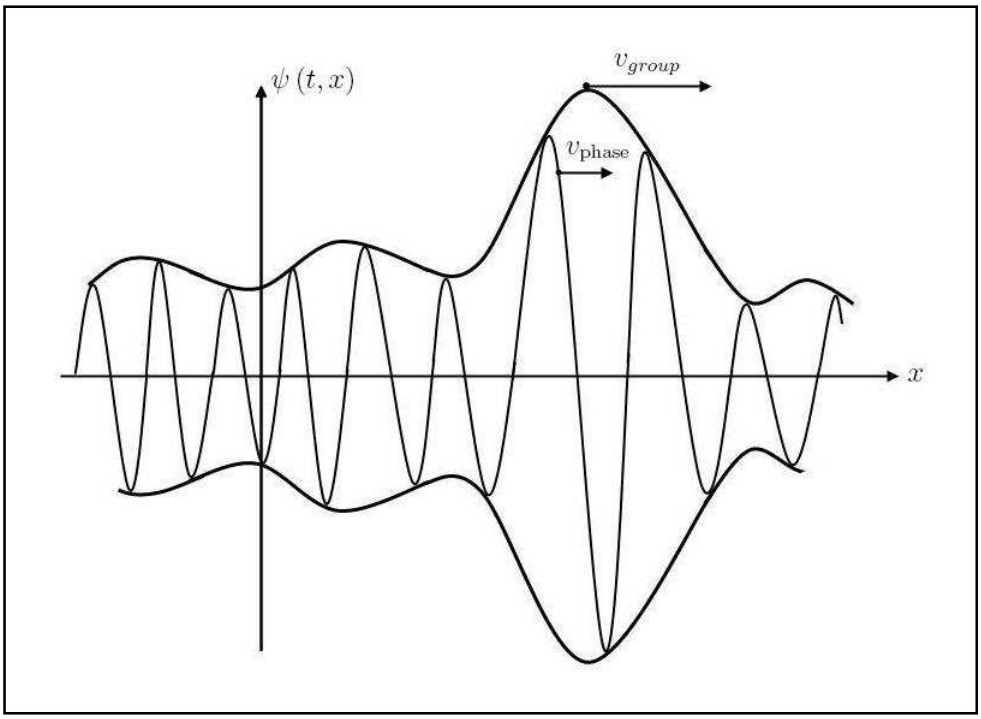

Figure 2.4: Wave packet: the phase velocities of different constituent plane waves suffer from dispersion whereas the group velocity accurately represents the motion of the enveloping function, i.e. the velocity of the peak.

Theorem 2.8 (Group velocity of wave packets)
Quantum mechanical wave packets $\psi(t,x)$, whose Fourier transform $\tilde{\psi}(k)$ is localized around a certain value k_0, move with the group velocity

$$v_{\text{group}} = \frac{d\omega}{dk}\Big|_{k=k_0} = 2\,v_{\text{phase}}$$

Proof:
The requirement of localization in the k-space can easily be fulfilled by a Gaussian distribution, like e.g.

$$\tilde{\psi}(k) \;=\; \text{const.} \;\times\; \exp\left(-\frac{\sigma^2(\mathrm{k}-\mathrm{k}_0)^2}{2}\right). \tag{2.107}$$

The dispersion relation, Eq. (2.106) we can expand as a Taylor series at k_0

$$\omega(k) \;=\; \omega(k_0) \;+\; \left.\frac{d\omega}{dk}\right|_{k=k_0} (k-k_0) \;+\; \cdots \;\cong\; \omega_0 \;+\; \omega_0'(k-k_0)\,, \tag{2.108}$$

where we have used the notation $\omega_0 = \omega(k_0)$, $\omega_0' = \left.\frac{d\omega}{dk}\right|_{k=k_0}$, and we may just keep the linear term due to the localized form of the packet in k-space, Eq. (2.107). With a change of variables $k \;\rightarrow\; k - k_0 = \bar{k}$ we can write the Fourier integral from Eq. (2.104) as

$$\psi\,(t,x) \;\cong\; \int\limits_{-\infty}^{\infty} \frac{d\bar{k}}{\sqrt{2\pi}}\, \tilde{\psi}\left(\bar{k}+k_0\right) \exp\left[i\left((\bar{k}+k_0)x - (\omega_0+\omega_0'\bar{k})t\right)\right]. \tag{2.109}$$

By examining the form of Eq. (2.109) at different times, e.g. at $t = 0$ and $t > 0$, we get

$$\psi\,(t=0,x) \;\;=\;\; \int \frac{d\bar{k}}{\sqrt{2\pi}}\, \tilde{\psi}\left(\bar{k}+k_0\right) \exp\left(i(\bar{k} \;+\; k_0)x\right), \tag{2.110}$$

$$\psi\,(t>0,x) \;\;\cong\;\; e^{i(k_0\omega_0'-\omega_0)t} \int \frac{d\bar{k}}{\sqrt{2\pi}}\, \tilde{\psi}\left(\bar{k}+k_0\right) \exp\left(i(\bar{k}+k_0)(x-\omega_0't)\right). \tag{2.111}$$

Except for the shift $x \;\rightarrow\; x - \omega_0' t$ the integrals in (2.110) and (2.111) are identical, thus

$$\psi\,(t,x) \;\cong\; e^{i(k_0\omega_0'-\omega_0)t}\, \psi\,(t, x-\omega_0' t)\;. \tag{2.112}$$

We conclude that after some time the wave packet propagated away from position x with the velocity $\omega_0' = v_{\text{group}}$. The phasefactor $\exp\left(i(k_0\omega_0' - \omega_0)t\right)$ in front of the integral can be ignored, since it will vanish in $|\psi|^2$. Finally, we simply calculate v_{group} using the dispersion relation (2.106) and find

$$v_{\text{group}} \;=\; \omega_0' \;=\; \frac{d\omega(k)}{dk} \;=\; \frac{d}{dk}\frac{\hbar k^2}{2m} \;=\; \frac{\hbar k}{m} \;=\; \frac{p}{m} \;=\; 2\,v_{\text{phase}} \qquad \text{q.e.d.} \tag{2.113}$$

2.8.2 Spreading of the Free Wave Packet

After having studied the motion of the wave packet, we now take a closer look at the localization of the particle associated with the wave packet. We again start from the general wave packet, from Eq. (2.104), but we use momentum and energy instead of wave number and frequency as variables

$$\psi\,(t,x) \;=\; \int\limits_{-\infty}^{\infty} \frac{dp}{\sqrt{2\pi\hbar}}\, \tilde{\psi}\,(p)\, \exp\left(\frac{i}{\hbar}\,(px - Et)\right). \tag{2.114}$$

We choose for the Fourier transform $\tilde{\psi}(p)$ a Gaussian distribution (on p-space)

$$\tilde{\psi}(p) = \underbrace{\left(\frac{\sigma}{\sqrt{\pi}\hbar}\right)^{1/2}}_{N} \exp\left(-\frac{\sigma^2(p-p_0)^2}{2\hbar^2}\right), \tag{2.115}$$

which ensures that, at an initial time $t = 0$, the wave packet is well localized (in x-space), i.e. σ is small[16]. We have also assumed that the Gaussian is normalized to one, which uniquely determines the normalization constant $N = \sqrt{\frac{\sigma}{\sqrt{\pi}\hbar}}$.

We then calculate the wave packet (Eq. 2.114)

$$\psi(t,x) = \frac{N}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp \, \exp\left(-\frac{\sigma^2(p-p_0)^2}{2\hbar^2}\right) \exp\left(\frac{i}{\hbar}(px - Et)\right). \tag{2.116}$$

Using $E = \frac{p^2}{2m}$ and the abbreviations

$$a := \frac{\sigma^2}{2\hbar^2} + i\frac{t}{2m\hbar}, \qquad b := \frac{\sigma^2 p_0}{2\hbar^2} + i\frac{x}{2\hbar}, \qquad c := \frac{\sigma^2 p_0^2}{2\hbar^2} \tag{2.117}$$

we get

$$\psi(t,x) = \frac{N}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp \, \exp\left(-a\left(p - \frac{b}{a}\right)^2 + \frac{b^2}{a} - c\right). \tag{2.118}$$

With a change of variables, $y = p - \frac{b}{a}$, and using the

$$\text{Gauss formula} \qquad \int_{-\infty}^{\infty} dy \, e^{-\alpha y^2} = \sqrt{\frac{\pi}{\alpha}}, \tag{2.119}$$

we arrive at a simple form for the Gaussian wave packet

$$\psi(t,x) = \frac{N}{\sqrt{2a\hbar}} \exp\left(\frac{b^2}{a} - c\right). \tag{2.120}$$

We are now interested in the probability density $\rho(t,x) = |\psi(t,x)|^2$ of this wave packet

$$|\psi(t,x)|^2 = \frac{N^2}{2\hbar}\frac{1}{|a|} \exp\left(2\mathrm{Re}\left(\frac{\mathrm{b}^2}{\mathrm{a}} - \mathrm{c}\right)\right). \tag{2.121}$$

Thus we calculate the constituent parts from the abbreviations a, b and c step by step

$$|a|^2 = a^* a = (\mathrm{Re(a)})^2 + (\mathrm{Im(a)})^2 = \left(\frac{\sigma^2}{2\hbar^2}\right)^2 + \left(\frac{\mathrm{t}}{2\mathrm{m}\hbar}\right)^2 = \left(\frac{\sigma^2}{2\hbar^2}\right)^2 \left[1 + \Delta^2\right], \tag{2.122}$$

[16]The width of the p-space distribution on the other hand is proportional to $1/\sigma$, which means that the momentum spread is high at $t = 0$.

where $\Delta := \frac{\hbar}{m\sigma^2}t$, and using $v = \frac{p_0}{m} = v_{\text{group}}$ we finally have

$$2\,\mathrm{Re}\left(\frac{\mathrm{b}^2}{\mathrm{a}} - \mathrm{c}\right) = 2\,\mathrm{Re}\left(\frac{\mathrm{b}^2\mathrm{a}^* - \mathrm{c}|\mathrm{a}|^2}{|\mathrm{a}|^2}\right) = -\frac{(\mathrm{x} - \mathrm{vt})^2}{\sigma^2(1+\Delta^2)}\,. \tag{2.123}$$

Altogether we find the following form for the **probability density of the Gaussian wave packet as a function of time**

$$|\psi\,(t,x)|^2 = \frac{1}{\sqrt{\pi}\,\sigma\sqrt{1+\Delta^2}}\,\exp\left(-\frac{(x-vt)^2}{\sigma^2(1+\Delta^2)}\right). \tag{2.124}$$

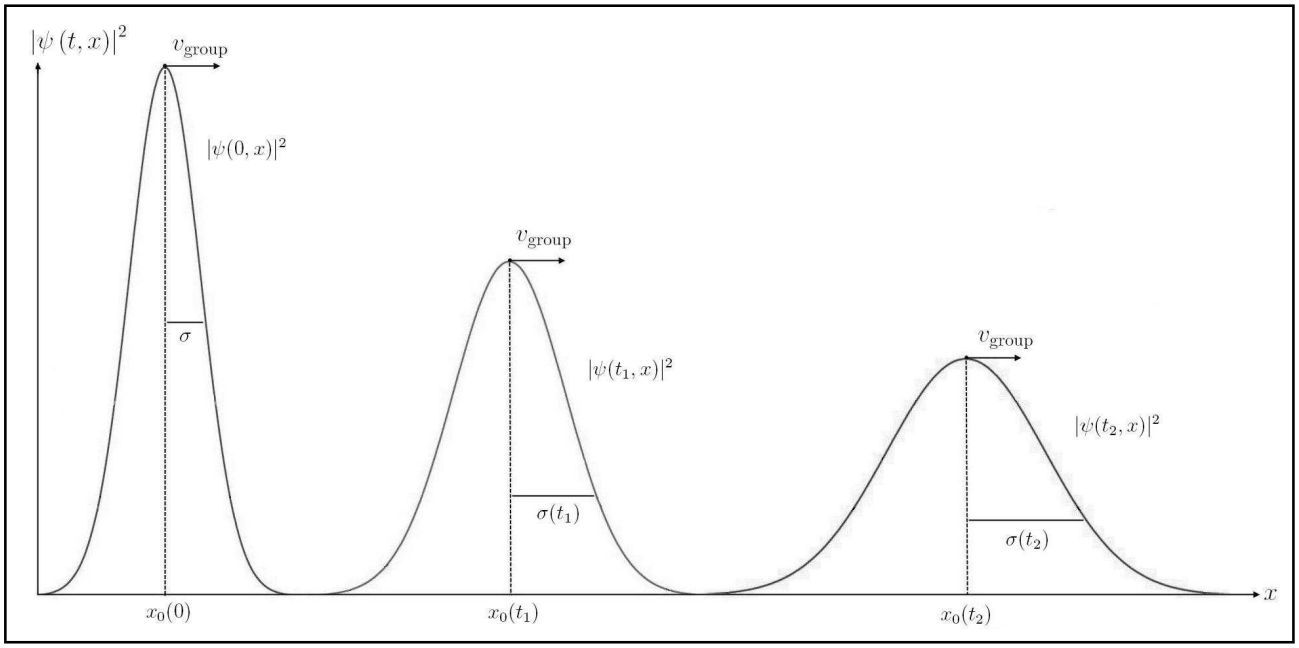

Figure 2.5: Spreading of the wave packet: As time passes, the envelope of the wave packet moves in the x-direction with velocity v_{group} and it gets more and more delocalized. Here $\sigma(t) := \sigma\sqrt{1+\Delta^2(t)}$

Result:

- The wave packet stays a Gaussian for all times, but its width, measured by $\sigma\sqrt{1+\Delta^2}$, increases with time, since $\Delta \propto t$. Thus the localizability of the particle represented by the wave packet decreases over time, which is termed the **spreading of the wave packet**, see Fig. 2.5.
- The maximum of the wave packet moves with $v_{\text{group}} = \frac{\hbar k}{m} = \frac{p_0}{m} = v_{\text{class}}\,.$
- The constituent plane waves of the superposition propagate with $v_{\text{phase}} = \frac{1}{2}v_{\text{group}}$.