

Introduction to Theoretical Physics: Quantum Mechanics

partly extracted from the lecture notes of
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Introduction

Quantum mechanics is of central importance for our understanding of nature. As we will see, even simple experiments show that the **classical deterministic approach with its well-defined properties of matter** is incorrect.

This is most obvious **at the microscopic scale**, in the regime of **atoms and elementary particles**, which can only be described with the help of quantum mechanics.

But of course **also the macroscopic world** is defined by quantum mechanics, which is important in phenomena like e.g. **a laser, an LED, superconductivity, ferro-magnetism, nuclear magnetic resonance (MRI in medicine), or even large objects like neutron stars.**

One of the central propositions of quantum mechanics is, that **only statements about probabilities** can be made, unlike in classical physics, where one can predict the behaviour of a system by solving the equations of motion.

The corresponding **equation of motion in quantum mechanics** is the Schrödinger's equation, which **describes** so-called **probability amplitudes** instead of deterministic locations.

Just like every other theory quantum mechanics cannot be *derived*, not any less than Newton's laws can be.

The development of the theory follows experimental observations,

If a theory does not only describe previous observations but can make own predictions, further experiments can be performed to verify their validity.

If these predictions were indeed correct, the theory is furthermore confirmed, however not “proven”,

If a prediction of a theory is, however, *not* correct, then the theory is *falsified*. The in many aspects at first very peculiar quantum mechanics has so far splendidly withstood all experimental examinations, unlike some previously proposed alternatives (with e.g. „hidden variables”).

In latest years there has been a rapid development in the application of experimentally increasingly well controllable, fundamental quantum mechanics, e.g. for quantum information science, with some spectacular experiments („quantum teleportation”), which specifically uses the non-local properties of quantum mechanics. Fundamental quantum mechanical phenomena are also increasingly interesting for specifically designed applications like quantum cryptography or quantum computers.

Literature

- R. SHANKAR, *Principles of Quantum Mechanics*, 1994.
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- J.L. BASDEVANT, J. DALIBARD, *Quantum Mechanics*, 2002.
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Failures of classical physics

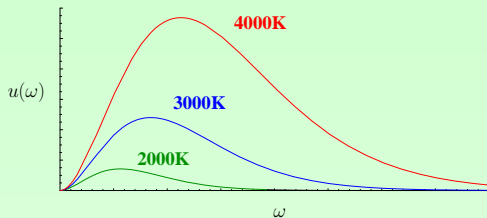


Blackbody radiation

At high temperatures matter (for example metals) emit a continuum radiation spectrum. The color they emit is pretty much the same at a given temperature independent of the particular substance.

An idealized description is the so-called blackbody model, which describes a perfect absorber and emitter of radiation.

In a blackbody, electromagnetic waves of all wavevectors \mathbf{k} are present. One can consider a wave with wavevector \mathbf{k} as an independent oscillator (mode).



Energy density $u(\omega)$ of blackbody radiation at different temperatures:

- The energy distribution $u(\omega)$ vanishes at small and large ω , there is a maximum in between.
- The maximum frequency ω_{max} (“color”) of the distribution obeys the law (Wien’s law) $\omega_{max} = \text{const. } T$

Classical understanding

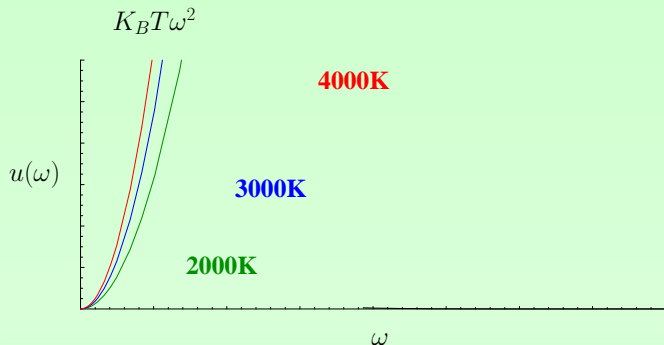
For a given frequency ω ($= 2\pi\nu$), there are many oscillators (modes) \mathbf{k} having that frequency. Since $\omega = c |\mathbf{k}|$ the number (density) $n(\omega)$ of oscillators with frequency ω is proportional to the surface of a sphere with radius ω/c , i. e.

$$n(\omega) \propto \omega^2 \quad (4.1)$$

The energy equipartition law of statistical physics tells us that at temperature T each mode is excited to the same energy $K_B T$. Therefore, at temperature T the energy density $u(\omega, T)$ at a certain frequency ω would be given by

$$u(\omega, T) \propto K_B T \omega^2 \quad (4.2)$$

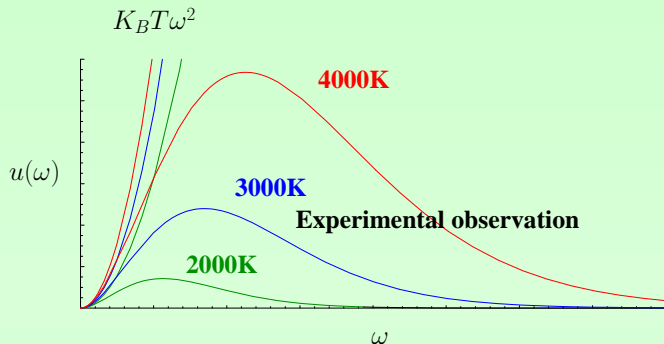
(Rayleigh hypothesis).



This agrees with experiments at small ω , but a large ω $u(\omega, T)$ must decrease again and go to zero. It *must* because otherwise the total energy

$$U = \int_0^{\infty} u(\omega, T) d\omega \quad (4.3)$$

would diverge !



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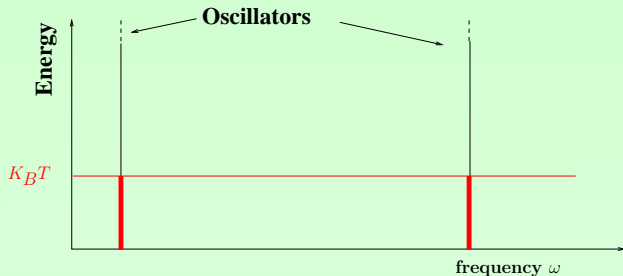
Planck's hypothesis:

The “oscillators” (electromagnetic waves), cannot have a continuous of energies. Their energies come in “packets” (quanta) of size $h \nu = \hbar \omega$.

$h \approx 6.6 \times 10^{-34} \text{ Joules sec}$ ($\hbar = \frac{h}{2\pi}$) Planck's constant.

At small frequencies, as long as $K_B T \gg \hbar \omega$, this effect is irrelevant. It will start to appear at $K_B T \sim \hbar \omega$: here $u(\omega, T)$ will start to decrease. And in fact, Wien's empiric observation is that at $\hbar \omega \propto K_B T$ $u(\omega, T)$ displays a maximum. Eventually, for $K_B T \ll \hbar \omega$ the oscillators are not excited at all, their energy is vanishingly small. A more elaborate theoretical treatment gives the correct functional form.

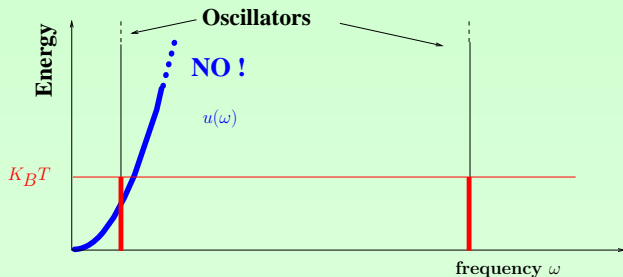
Average energy of “oscillators”



(A) Classical behavior:

Average energy of oscillator $\langle E \rangle = K_B T$.

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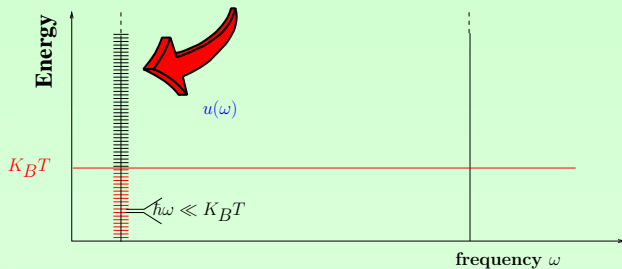


(A) Classical behavior:

Average energy of oscillator $\langle E \rangle = K_B T$.

\Rightarrow Distribution $u(\omega) \propto K_B T \omega^2$ at all frequencies!

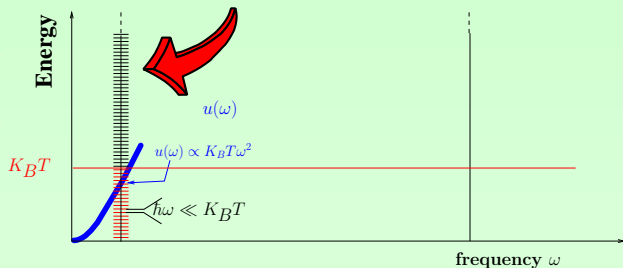
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(B) Quantum behavior: Energy quantisation

Small ω : Like classical case: oscillator is excited up to $\langle E \rangle \approx K_B T$.

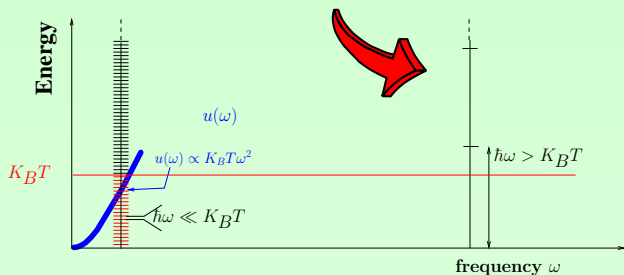
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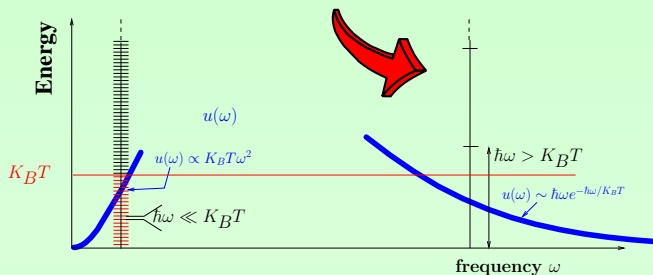
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(B) Quantum behavior: Energy quantisation

Large ω : first excited state ($E = 1 * \hbar\omega$) is occupied with probability $e^{-\hbar\omega/K_B T}$ (Boltzmann Factor): $\Rightarrow \langle E \rangle \approx \hbar\omega e^{-\hbar\omega/K_B T}$

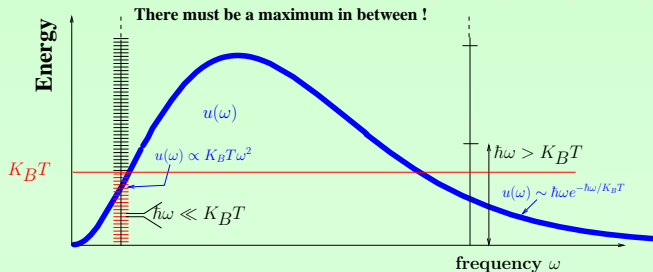
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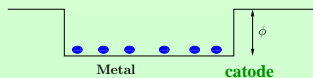
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Photoelectric effect

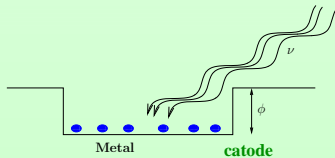
Photoelectric effect

Electrons in a metal are confined by an **energy barrier** (work function) ϕ .



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One way to extract them is to shine light onto a metallic plate.
Light transfers an energy E_{light} to the electrons.

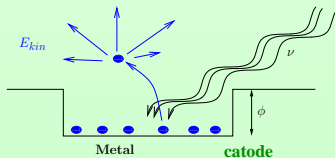


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Photoelectric effect

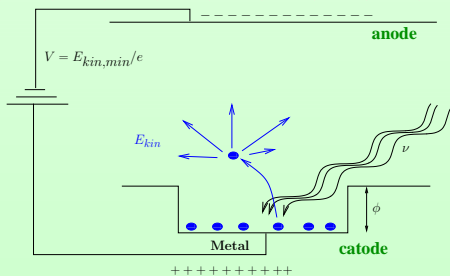
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By measuring E_{kin} , one can get E_{light} .



Photoelectric effect

examples:

Classically, we would expect the total energy transferred to an electron $E_{light} = \phi + E_{kin}$ to be **proportional to the radiation intensity**.

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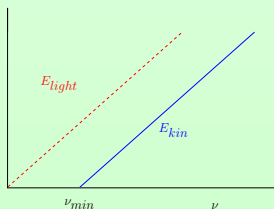
Photoelectric effect

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Classically, we would expect the total energy transferred to an electron $E_{light} = \phi + E_{kin}$ to be **proportional to the radiation intensity**. The experimental results give a different picture: while the **current** (i. e. the number of electrons per second expelled from the metal) is **proportional to the radiation intensity**,

E_{light} is **proportional to the frequency of light:**

$$E_{light} = h \nu \quad (4.4)$$



Summary: Planck's energy quantum

The explanation of Blackbody radiation and of the Photoelectric effect are explained by Planck's idea that light carries energy only in “quanta” of size

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Summary: Planck's energy quantum

The explanation of Blackbody radiation and of the Photoelectric effect are explained by Planck's idea that light carries energy only in “quanta” of size

$$E = h\nu \quad (4.5)$$

This means that light is **not continuous** object, but rather its constituent are **discrete: the photons**.

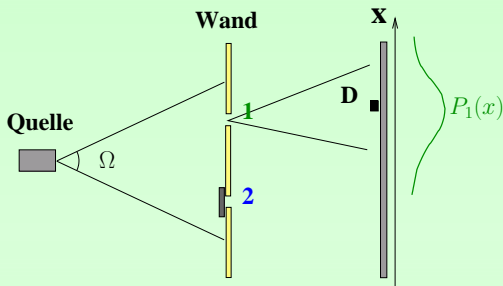
Waves and particles

In this lecture we don't want to talk about the historic development of quantum mechanics with all its detours, instead we will learn about several key experiments, where the failure of classical physics is especially evident and that led to formulations of quantum mechanics. However, as said above, quantum mechanics cannot be „derived“, it can only be made plausible. The most drastic observation that led to the abandonment of the classical approach were, that *all matter and all radiation has simultaneously wave-like and particle-like properties.*

This is especially clear in the so-called double-slit experiment. In aforementioned experiment particles or light is sent towards a wall with two slits. Behind this wall is a detector screen.

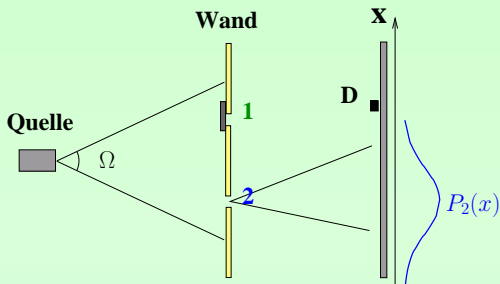
The double slit experiment with classical particles

Classical particles (e.g. spheres)



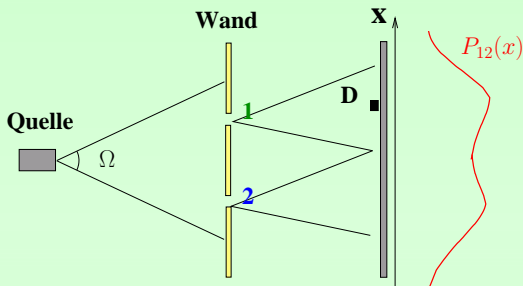
1) Only slit 1 is open: this yields the distribution $P_1(x)$

Classical particles (e.g. spheres)



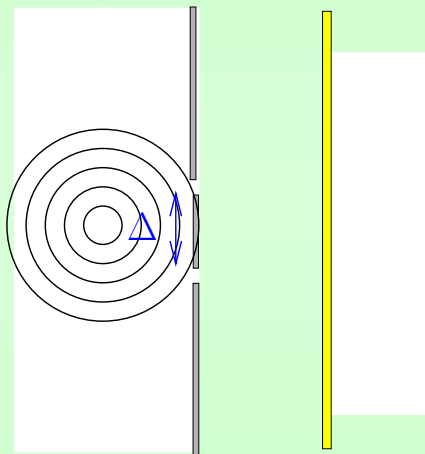
- 1) Only slit 1 is open: this yields the distribution $P_1(x)$
- 2) Only slit 2 is open: this yields the distribution $P_2(x)$

Classical particles (e.g. spheres)

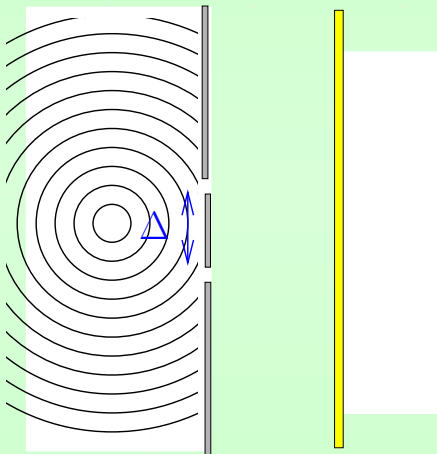


- 1) Only slit 1 is open: this yields the distribution $P_1(x)$
- 2) Only slit 2 is open: this yields the distribution $P_2(x)$
- 3) Both slits are open: this yields the distribution $P_{12}(x)$, namely simply the sum $P_{12}(x) = P_1(x) + P_2(x)$ of both prior distributions.

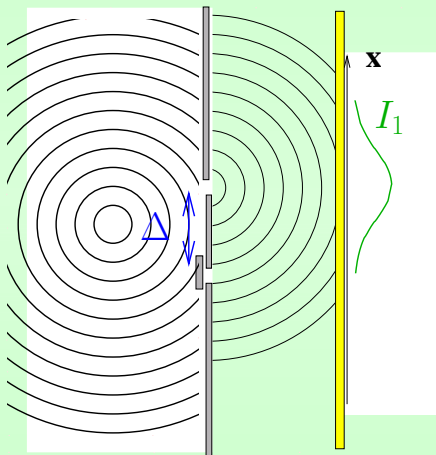
Water waves



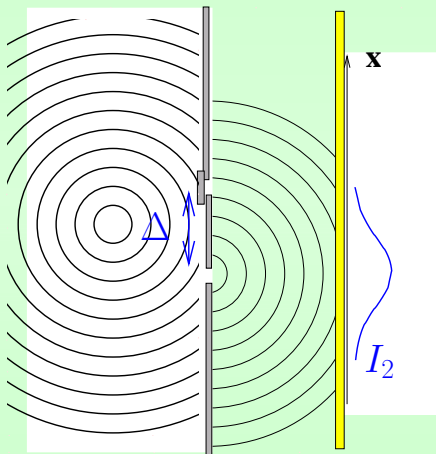
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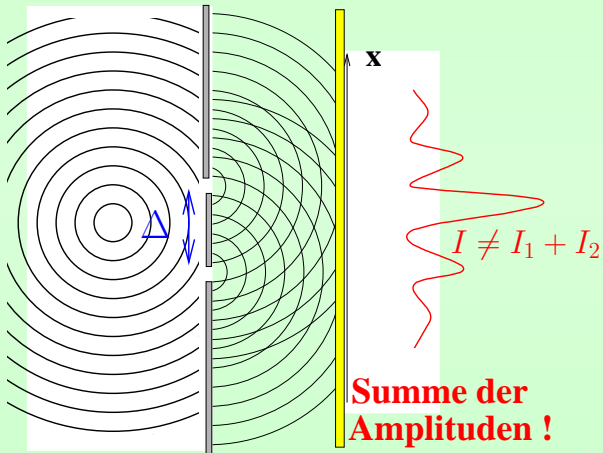
Water waves



Water waves



Water waves



Mathematical description

We use $e^{i\phi} = \cos \phi + i \sin \phi$,

Momentary amplitude:

$$A_1 = \operatorname{Re} (a_1 e^{i\alpha_1} e^{i\omega t})$$

$$A_2 = \operatorname{Re} (a_2 e^{i\alpha_2} e^{i\omega t})$$

$$A_{12} = \operatorname{Re} (a_1 e^{i\omega t + i\alpha_1} + a_2 e^{i\omega t + i\alpha_2})$$

only slit 1 is open

only slit 2 is open

both slits are open

The relation to the measured, averaged over time, intensity is

$$I_1 = \overline{(\operatorname{Re} a_1 e^{i\omega t + i\alpha_1})^2} = \frac{1}{2} |a_1|^2$$

$$I_2 = \overline{(\operatorname{Re} a_2 e^{i\omega t + i\alpha_2})^2} = \frac{1}{2} |a_2|^2$$

$$I_{12} = \overline{(\operatorname{Re} (a_1 e^{i\omega t + i\alpha_1} + a_2 e^{i\omega t + i\alpha_2}))^2} = \frac{|a_1|^2 + |a_2|^2}{2} + |a_1| |a_2| \cos(\alpha_1 - \alpha_2) \\ = I_1 + I_2 + |a_1| |a_2| \cos(\alpha_1 - \alpha_2).$$

The term with the \cos is the *interference term*, that depends on the **phase difference** $\alpha_1 - \alpha_2$, that comes from the path difference.

Light

The usual and very successful description of **light** in the macroscopic world is that of a **wave**, with electric and magnetic fields.

The **particle-like description via photons**, made necessary by experiments, was a revolution.

Light consists of photons

Before the review of the double slit experiments, here some more **early experiments** that show the **particle nature of light**.

Details in Sec. 4

- The temperature dependent spectrum of a so-called black body cannot be understood classically. With the classical wave-like nature of light, the intensity of the spectrum would diverge at high frequencies. The energy density of the electromagnetic field would be infinite!

The explanation for the actually observed spectrum was found by Planck in 1900 (on the same day, when he received the exact experimental results!), by postulating that

light is only emitted in fixed quantities of the energy $E = h\nu$.

These „quanta“, later called photons, gave quantum theory its name. This postulate was a sheer „act of desperation“ of Planck and was viewed with great scepticism. Einstein even called it „insane“.

- At the **photoelectric effect** a photon with frequency ν emits an electron from a metal, that electron then has the **kinetic energy** $h\nu - \Phi$ where Φ is the work of emission. Therefore exists a threshold for the frequency of the photon, below which no electrons can be emitted.

Classically one would expect, that at every photon frequency more and more electrons would be emitted, increasingly with higher light intensity. Instead the intensity of the light only determines the *number* of electrons that are emitted, not their kinetic energy and has therefore no influence on whether this process is even allowed.

With the Light Quantum Hypothesis in 1905, Einstein could finally explain the photoelectric effect. This was this publication, for which he was awarded the Nobel Prize in 1921.

- Also the Compton effect, with the scattering of light on electrons, can only be explained via the introduction of photons.
- Even more directly one can notice the particle properties of light with Geiger counters, photo multipliers or with CCDs (digital cameras!). Interestingly one can even notice rapidly changing spot-like brightness fluctuations on a weakly illuminated wall with the bare eye. This is caused by the fluctuation of the amount of photons observed, which can be perceived from approximately 10 per 100msec onwards.

Light has a wave-like nature

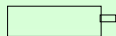
One can clearly see the wave-like nature of light with the double slit experiment:

Setup and result regarding the intensities behave exactly like the experiment with water waves.

In Maxwell's theory is the **intensity of light proportional to the square of the amplitude** of the electric field $I \sim \vec{E}^2$, therefore of the same structure as water waves, only that the electric and magnetic field now affect the amplitude.

Light: particles or waves?

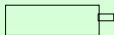
Einzelne Photonen?



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Light: particles or waves?

**Einzelne
Photonen?**

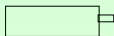


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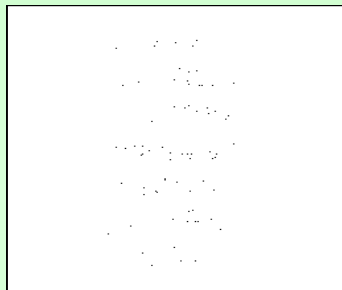
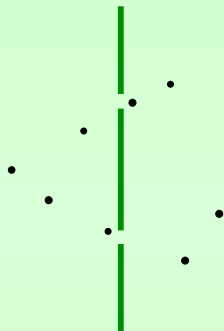


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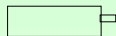


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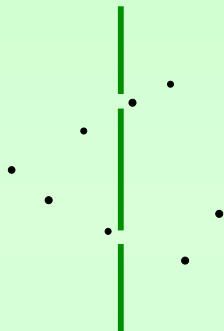


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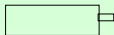


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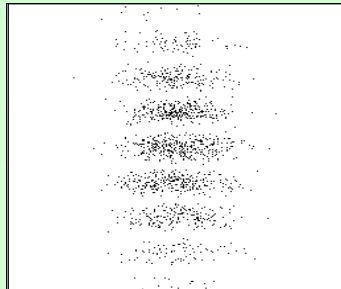
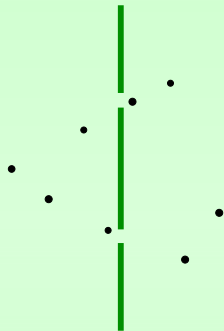


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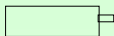


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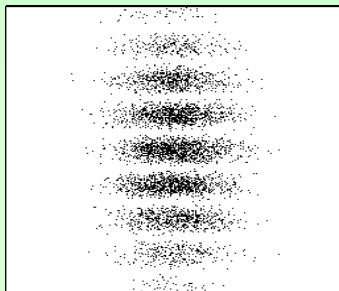


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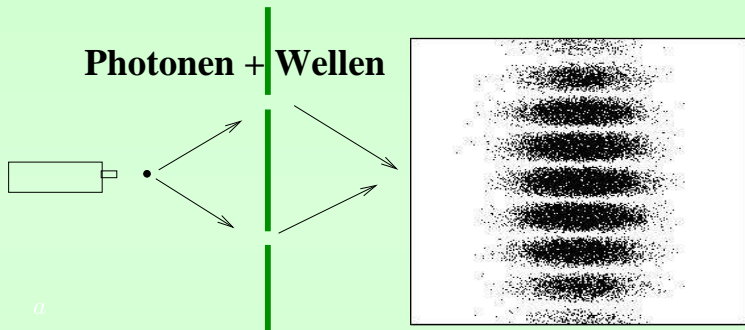
Einzelne Photonen?



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Light: particles or waves?



Completely different, however, than with the water waves is the impingement of the light on the screen: the photons hit the surface *individually*, each with the energy $h\nu$, but still create an interference pattern, when 2 slits are open!

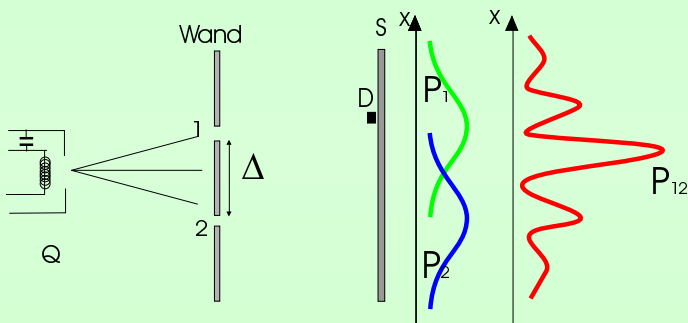
Electrons

The problem of the **wave and particle nature** is even more obvious in the case of **matter, like electrons or atoms**.

The „particle nature” is here very clear. For example one can determine both charge and mass for a single electron.

Interference of electrons

The behaviour on the double slit shows yet again a wave-like nature (see figure ??)!



Double slit experiment with electrons.

Experimental observations:

- 1 The electrons arrive individually (just like classical particles) at the detector.

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- 1 The electrons arrive individually (just like classical particles) at the detector.
- 2 In dependence of the location on the detector screen is a varying count rate of the electrons.
- 3 The quantity measured in the experiment is the distribution of the electrons on the detector screen. This corresponds to the impingement probability on different locations of the screen.

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- 1 The electrons arrive individually (just like classical particles) at the detector.
- 2 In dependence of the location on the detector screen is a varying count rate of the electrons.
- 3 The quantity measured in the experiment is the distribution of the electrons on the detector screen. This corresponds to the impingement probability on different locations of the screen.
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The same behaviour is also observed with neutrons, atoms and even fullerene molecules!

de Broglie wavelength

The interference result shows us, that both photons as well as electrons (just like every microscopic particle) have a wave-like nature.

For a given momentum p is the spatial periodicity of these waves given by the

de-Broglie-wavelength

$$\lambda = \frac{2\pi}{k} = \frac{h}{p} \quad (5.1)$$

This length scale λ appears at the double slit experiment, as well as e.g. at the scattering of particles with momentum p in a crystal.

As we will see in the next chapters, free electrons can be described in quantum mechanics by a probability amplitude in the form of a plane wave e^{ipx} .

examples: Quantum mechanical effects are of increasing importance below : a length scale of the order of magnitude of the de-Broglie-wavelength λ . Here some examples for length scales:

$$\text{Protonen: } \lambda \simeq \frac{0.28 \text{ \AA}}{\sqrt{E_{kin}/\text{eV}}}$$

$$\text{Elektronen: } \lambda \simeq \frac{12 \text{ \AA}}{\sqrt{E_{kin}/\text{eV}}} \quad (5.2)$$

$$\text{Photonen: } \lambda \simeq \frac{380 \text{ \AA}}{\sqrt{E_{kin}/\text{eV}}}$$

The wave function and Schrödinger equation



Probability density and the wave function

In Sec. 5 we have seen that the trajectory of a particle is **not deterministic**, but described by a **probability distribution amplitude**.

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This probability (which depends of course on ΔV) is given in terms of the **probability density** $P_t(\mathbf{r})$, as $W = P_t(\mathbf{r})\Delta V$

Obviously, the total probability of finding the particle within a volume V is given by

$$\int_V P_t(\mathbf{r})d^3\mathbf{r} .$$

As discussed in Sec. 5, the relevant (i. e. additive) quantity for a given particle is its **probability amplitude** $\Psi(t, \mathbf{r})$. This is a complex function, and the probability density P is given by

$$P_t(\mathbf{r}) = |\Psi(t, \mathbf{r})|^2 . \quad (6.1)$$

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As discussed in Sec. 5, it is possible to predict the time evolution of Ψ , which is what we are going to do in the present section.

To do this, we will start from the wave function of light, whose properties we already know from classical electrodynamics, and try to extend it to matter waves.

Wave equation for light

The wave function describing a **free electromagnetic wave**, can be taken, for example, as the amplitude of one of its two constituent fields, E or B , i. e. it has the form

$$\Psi = E_0 e^{i\mathbf{k}\cdot\mathbf{r} - i\omega_k t} \quad (6.2)$$

Planck's quantisation hypothesis was that light of a certain frequency ω comes in quanta of energy

$$E = \hbar \omega \quad (6.3)$$

(Or taking $\nu = \omega/(2\pi)$, $E = h \nu$), with Planck's constant

$$h = 2\pi \hbar \approx 6.6 \times 10^{-34} \text{ Joules sec} \quad (6.4)$$

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From the energy we can derive the momentum. Here we use, the relation between energy E and momentum p for photons, which are particles of zero rest mass and move with the velocity of light c :¹

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From 6.3 we thus obtain

$$p = \frac{\hbar\omega}{c} = \hbar k = \frac{h}{\lambda} \quad (6.6)$$

which is precisely the De Broglie relation between momentum and wavelength of a particle discussed in Sec. 5.

Here, we have used the **dispersion relation**

$$\omega = c|k| \quad (6.7)$$

Heuristic derivation of the wave function for massive particles

With the assumption that matter particles (i. e. particle with a nonzero rest mass such as electrons, protons, etc.) with a given momentum and energy behave as waves, their wave function will be described by a form identical to [6.2](#), however with a **different dispersion relation**.

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The latter can be derived by starting from the energy-momentum relation, which instead of [6.5](#) reads (in the nonrelativistic case)

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Applying Planck's [6.3](#) and De Broglie relations [6.6](#), we readily obtain the **dispersion relation for nonrelativistic massive particles**

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \quad (6.9)$$

Wave equations

One property of electromagnetic waves is the **superposition principle**:
If Ψ_1 and Ψ_2 are two (valid) wave functions, any linear combination
 $a_1\Psi_1 + a_2\Psi_2$ is a valid wave function.

Due to this linearity property, any valid wave function must satisfy a
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notice that Ψ ^{6.2} (valid both for matter as well as light) is an **eigenfunction** of the differential operators ∇ and $\partial/\partial t$, i. e.

$$-i\nabla \Psi = k \Psi \quad i \frac{\partial}{\partial t} \Psi = \omega \Psi \quad (6.11)$$

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$$-i\nabla \Psi = k \Psi \quad i \frac{\partial}{\partial t} \Psi = \omega \Psi \quad (6.11)$$

Replacing 6.11 in 6.10, we see that the latter is equivalent to the dispersion relation

$$\omega^2 = c^2 k^2 \quad (6.12)$$

This immediately suggests to use the dispersion relation [6.9](#) combined with the relation [6.11](#) to write down the corresponding analogous of [6.10](#) for massive particles:


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$$\left(i\hbar \frac{\partial}{\partial t} - \frac{1}{2m} (-i\hbar \nabla)^2 \right) \Psi = 0 \quad (6.13)$$

Which is the **(time-dependent) Schrödinger** equation for massive (nonrelativistic) free particles.

Potential

For a particle moving in a **constant potential** (i.e. t - and \mathbf{r} -independent) V , the dispersion relation [6.8](#) is replaced with $E = \frac{p^2}{2m} + V$, and [6.13](#) acquires a corresponding term $V \Psi$ on the l.h.s.

¹This can be understood if one assumes piecewise constant potentials V_i , and requires that locally the equation for wave equation should only depend on the local V_i . In the end, one takes the limit of a continuous $V(t, \mathbf{r})$ 


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The guess by Schrödinger was to formally do the same also for a t - and \mathbf{r} -dependent potential ¹ $V(t, \mathbf{r})$, yielding the complete **time-dependent Schrödinger equation**

$$i\hbar \frac{\partial \Psi}{\partial t} = \underbrace{\left(-\frac{\hbar^2}{2m} \nabla^2 + V(t, \mathbf{r}) \right)}_{\hat{H}} \Psi \quad (6.14)$$

for a nonconstant potential [6.2](#) is no longer a solution of [6.14](#).

¹This can be understood if one assumes piecewise constant potentials V_i , and requires that locally the equation for wave equation should only depend on the local V_i . In the end, one takes the limit of a continuous $V(t, \mathbf{r})$ 

The differential operator on the r.h.s. of [6.14](#) is termed **Hamilton operator** \hat{H} . Symbolically, thus, the Schrödinger equation is written as

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi . \quad (6.15)$$

In general, Ψ can belong to a larger vector space (such as a function in $3N$ variables for N particles or contain further degrees of freedom, such as spin).

Combining the relations (6.3) and (6.6), we see that energy and momentum, which were variables in classical physics, become now **differential operators**

$$E \rightarrow i\hbar \frac{\partial}{\partial t} \quad \mathbf{p} \rightarrow -i\hbar \nabla . \quad (6.16)$$

This is one important aspect of quantum mechanics, which we will discuss further below, namely the fact that **physical quantities** become **linear operators**.

Time-independent Schrödinger equation

Time-independent Schrödinger equation

We consider in the following a stationary (i. e. time-independent) potential $V(\mathbf{r})$ and look for solution of [6.14](#) in the form (separation of variables)

$$\Psi(t, \mathbf{r}) = f(t)\psi(\mathbf{r}) \quad (6.17)$$

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dividing by $f(t)\psi(\mathbf{r})$, [6.14](#) becomes

$$\underbrace{\frac{1}{f(t)} i\hbar \frac{df(t)}{dt}}_{\text{independent of } \mathbf{r}} = \underbrace{\frac{1}{\psi(\mathbf{r})} \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \psi(\mathbf{r})}_{\text{independent of } t} \quad (6.18)$$

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[6.18](#) thus splits into two equations, the first being easy to solve

$$i\hbar \frac{df(t)}{dt} = E f(t) \Rightarrow f(t) = f_0 \exp\left(-i \frac{E t}{\hbar}\right) \quad (6.19)$$

Time-independent Schrödinger equation

the second one is the **time-independent Schrödinger equation**

$$\underbrace{\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right)}_{\hat{H}} \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (6.20)$$

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$$\underbrace{\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right)}_{\hat{H}} \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (6.20)$$

This is the equation for a wave function of a particle **with a fixed value of the energy**.

It is one of the most important equations in quantum mechanics and is used, e.g., to find atomic orbitals.

Schrödinger equation: ideas

These results suggest us some ideas that we are going to meet again later

- Physical quantities (observables), are replaced by **differential operators**.

Here we had the case of energy E and momentum \mathbf{p} :

$$\begin{aligned} E &\rightarrow i\hbar\frac{\partial}{\partial t} = \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \\ \mathbf{p} &\rightarrow \hat{\mathbf{p}} = -i\hbar\nabla \end{aligned} \quad (6.21)$$

The “hat” $\hat{}$ distinguishes an operator from its corresponding value.

²also called eigenstates

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- [6.20](#) has the form of an **eigenvalue equation** similar to the one we encounter in linear algebra.

The solutions of [6.20](#) are, thus, **eigefunctions²** of \hat{H}

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The solutions of [6.20](#) are, thus, **eigefunctions²** of \hat{H}

- Solutions of [6.20](#) are called **stationary states**, since their time evolution is given by [6.18](#) with [6.19](#), so that the probability density $|\Psi(t, \mathbf{r})|^2$ is time-independent.

²also called eigenstates

Ways to solve the time-dependent Schrödinger equation

Not any wave function will have the separable form $\psi(x,t) = \psi(x)\phi(t)$ (6.17). However, any wave function can be written as a **linear combination** of such terms.

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This is the most common approach used to solve the time-dependent Schrödinger equation. We will discuss it again later.

Normalisation

Due to the linearity of 6.20, its solution can be always multiplied by a constant.

An important point in quantum mechanics is that **two wave functions differing by a constant describe the same physical state.**

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An important point in quantum mechanics is that **two wave functions differing by a constant describe the same physical state.**

The value of the constant can be (partly) restricted by the condition that the **wavefunction is normalized.**

This is obtained by normalizing the probability density (6.1), i. e. by requiring that the total probability is 1. This gives the **normalisation condition**

$$\langle \psi | \psi \rangle \equiv \int |\psi(\mathbf{r})|^2 d^3\mathbf{r} = 1 . \quad (6.22)$$

It is not strictly necessary, but useful, to normalize the wave function. If the wave function is not normalized, however, one has to remember that the probability density $\rho(\mathbf{r})$ for finding a particle near \mathbf{r} is not merely $|\psi(\mathbf{r})|^2$ but

$$\rho(\mathbf{r}) = \frac{|\psi(\mathbf{r})|^2}{\langle \psi | \psi \rangle} \quad (6.23)$$

⋮

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Notice that even after normalisation the constant is not completely determined, as one can always multiply by a number of modulus 1, i. e. a **phase** $e^{i\alpha}$.

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Notice that even after normalisation the constant is not completely determined, as one can always multiply by a number of modulus 1, i. e. a **phase** $e^{i\alpha}$.

Finally, notice that not all wave functions are normalizable. In some cases the integral [6.22](#) may diverge. This is for example the case for free particles [6.2](#). We will discuss this issue later.

examples:

Summary of important concepts

(1) Wave-particle dualism

Objects (electrons, electromagnetic waves) are both **Waves and Particles**:

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Waves: Delocalized, produce interference

Particles: localized, quantized

Reconciling both aspects:

complex wave function $\Psi(t, \mathbf{r}) \rightarrow$ interference

probability density $\rho(\mathbf{r}) \propto |\Psi(t, \mathbf{r})|^2$

(2) New description of physical quantities

Physical quantities become **differential operators** on $\Psi(t, \mathbf{r})$:

$$\mathbf{p} \rightarrow -i\hbar\nabla \quad E \rightarrow i\hbar\frac{\partial}{\partial t} \quad (6.24)$$

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This comes by combining

(a) electromagnetic waves:

$$\mathbf{k} \rightarrow -i\nabla \quad \omega \rightarrow i\frac{\partial}{\partial t}$$

(b) de Broglie, Planck

$$\hbar\mathbf{k} = \mathbf{p} \quad \hbar\omega = E$$

(3) Wave equation for Ψ : Schrödinger equation

Combining 6.24 with classical energy relation

$$E = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r})$$

yields **Schrödinger equation**

$$i\hbar \frac{\partial}{\partial t} \Psi = \left(-\hbar^2 \frac{\nabla^2}{2m} + V(\mathbf{r}) \right) \Psi \equiv \hat{H} \Psi \quad (6.25)$$

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same idea as for electromagnetic waves:

$$E^2 = c^2 \mathbf{p}^2 \quad \rightarrow \quad \frac{\partial^2}{\partial t^2} \Psi = c^2 \nabla^2 \Psi$$

(4) Time independent Schrödinger equation

Separable solution of 6.25:

$$\Psi(t, \mathbf{r}) = e^{-iEt/\hbar} \psi(\mathbf{r})$$

Eigenfunction of the energy operator.

(4) Time independent Schrödinger equation

Separable solution of 6.25:

$$\Psi(t, \mathbf{r}) = e^{-iEt/\hbar} \psi(\mathbf{r})$$

Eigenfunction of the energy operator.

Requires solution of eigenvalue equation

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

which determines **Energy levels and wavefunctions**

Basic potential problems

Next we will solve the time independent Schrödinger equation 6.20 for some basic potential problems. We will only treat one-dimensional problems in the examples.

Boundary conditions for the wave function

First we derive the boundary conditions for the position-space wave function for Eigenstates of \hat{H} . First let's assume the one-dimensional case.

1) The wave function $\psi(x)$ is always continuous.

Proof: Let's assume
$$\int_{x_0-\varepsilon}^{x_0+\varepsilon} \left(\frac{d}{dx} \psi(x) \right) dx = \psi(x_0 + \varepsilon) - \psi(x_0 - \varepsilon) .$$

In the case that ψ is not continuous at x_0 , the right side would not vanish for $\varepsilon \rightarrow 0$. This, however, would imply that $\frac{d}{dx} \psi(x) \propto \delta(x - x_0)$ and

the kinetic energy would diverge:

$$\begin{aligned}
 E_{kin} &= \frac{-\hbar^2}{2m} \int_{-\infty}^{\infty} \psi^*(x) \frac{d^2}{dx^2} \psi(x) dx \\
 &= \frac{+\hbar^2}{2m} \int_{-\infty}^{\infty} \left(\frac{d}{dx} \psi^*(x) \right) \cdot \left(\frac{d}{dx} \psi(x) \right) dx = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left| \frac{d}{dx} \psi(x) \right|^2 dx \\
 &\propto \int_{-\infty}^{\infty} \delta(x - x_0) \cdot \delta(x - x_0) dx = \delta(0) = \infty \quad .
 \end{aligned}$$

Since the kinetic energy is finite, $\psi(x)$ must therefore be continuous everywhere.

2) The derivative $\frac{d\psi}{dx}$ is continuous for infinite potentials.

We integrate the Schrödinger equation from $x_0 - \varepsilon$ to $x_0 + \varepsilon$

$$-\frac{\hbar^2}{2m} \int_{x_0-\varepsilon}^{x_0+\varepsilon} \frac{d^2}{dx^2} \psi(x) dx = - \int_{x_0-\varepsilon}^{x_0+\varepsilon} V(x) \psi(x) dx + E \int_{x_0-\varepsilon}^{x_0+\varepsilon} \psi(x) dx . \quad (7.1)$$

For a finite potential $V(x)$ the right side of equation 7.1 vanishes in the limit $\varepsilon \rightarrow 0$, since $\psi(x)$ has no δ -contributions, otherwise the kinetic energy would diverge.

We obtain:

$$\lim_{\varepsilon \rightarrow 0} -\frac{\hbar^2}{2m} [\psi'(x_0 + \varepsilon) - \psi'(x_0 - \varepsilon)] = 0 \quad (7.2)$$

$\frac{\partial}{\partial x} \psi(x)$ is therefore continuous.

3) Jump in the derivative of ψ for potentials with δ -contribution

If $V(x)$ has δ -contributions $V(x) = C \cdot \delta(x - x_0) +$ (finite contributions), then

$$\int_{x_0-\varepsilon}^{x_0+\varepsilon} V(x) \psi(x) dx = \int_{x_0-\varepsilon}^{x_0+\varepsilon} C \cdot \delta(x - x_0) \psi(x) dx = C \psi(x_0)$$

Such a potential is used for example to describe potential barriers.

Therefore comes from **7.1** a *jump in the derivative of $\psi(x)$* :

$$\lim_{\varepsilon \rightarrow 0} \left(\psi'(x_0 + \varepsilon) - \psi'(x_0 - \varepsilon) \right) = \frac{2m}{\hbar^2} C \psi(x_0) \quad (7.3)$$

4) The wave function vanishes for infinite potentials

If $V(x) = \infty$ in an interval $x \in (x_a, x_b)$, then the wave function vanishes in this interval, since the potential energy would be infinite.

5) Discontinuity of $\frac{d\psi}{dx}$ on the edge of an infinite potential

If $V(x) = \infty$ in an interval $x \in (x_a, x_b)$, then the wave function is zero in the interval and continuous everywhere else, however, the derivative will generally not be continuous at the boundaries of the interval.

Boundary conditions for three-dimensional problems

From similar considerations we obtain for three dimensions, that the wave function and all partial derivatives must be continuous everywhere, when the potential is finite everywhere. Further general properties of the wave function will be discussed later.

Constant potential

Especially important for potential problems is the case, that the potential is *constant* in an interval. We will treat the one-dimensional problem. Let's therefore assume

$$V(x) = V = \text{const.} \quad \text{für } a < x < b .$$

In this interval the Schrödinger equation 6.20 reads as

$$-\frac{\hbar^2}{2m} \psi''(x) = (E - V) \psi(x) \quad (7.4)$$

(Vibration equation), with the general solution

Solution of the Schrödinger equation for a constant potential

$$\psi(x) = a_1 e^{qx} + b_1 e^{-qx} \quad (7.5a)$$

$$= a_2 e^{ikx} + b_2 e^{-ikx} \quad (7.5b)$$

$$= a_3 \cos(kx) + b_3 \sin(kx), \quad (7.5c)$$

$$\text{with } k^2 = -q^2 = \frac{2m}{\hbar^2} (E - V) \quad (7.5d)$$

These three solutions are *equivalent* !

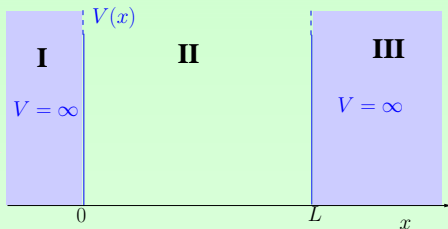
If $E < V$, then q is real-valued, and the formulation of the first line is convenient. The wave function $\psi(x)$ then generally has exponentially increasing and decreasing contributions in the interval $[a, b]$

If $E > V$, then k is real-valued, and the second or third line is convenient, depending on the boundary conditions. The wave function exhibits oscillatory behaviour in the interval $[a, b]$.

Bound states in a potential well

Infinite potential well

The potential well with infinite walls, shown in figure 2, can be interpreted as a highly idealized solid state. The electrons feel a constant potential in the solid and are prevented from leaving by the infinite walls.



Infinite potential well

The potential 2 is

$$V(x) = \begin{cases} V_0 := 0 & \text{for } 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

Therefore exist three qualitatively different areas, shown in the sketch. It is often times practical for such potential problems to first find general solutions for the wave function in the areas and then connect them, according to the existing boundary conditions.

We find for the infinite potential well:

Areas I & III: ² Here is $V(x) = \infty$ and therefore $\psi(x) \equiv 0$, since otherwise

$$E_{pot} = \int V(x) |\psi(x)|^2 dx = \infty$$

Area II: 2 Here is the *potential constant*.

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1. Attempt: We set $E < V_0 = 0$ and use 7.5a:

$$\psi(x) = a e^{qx} + b e^{-qx}$$

with real-valued $q = \sqrt{\frac{2m}{\hbar^2} (V_0 - E)}$.

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The continuity of the wave function at $x = 0$ demands $\psi(0) = 0$, thus $a = -b$. The continuity at $x = L$ demands $\psi(L) = 0$, thus $e^{qL} - e^{-qL} = 0$. From this we obtain $q = 0$ and with this $\psi(x) = a(e^0 - e^0) \equiv 0$. We therefore find no solution for $E < V_0$!

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2. Attempt: We set $E > V_0$ and use (due to the boundary conditions)

7.5c:

$$\psi(x) = a \sin kx + b \cos kx \quad (7.6)$$

with $k = \sqrt{\frac{2m(E - V_0)}{\hbar^2}}$, $a, b \in \mathbb{C}$.

The wave function must satisfy several conditions:

- The continuity of the wave function defines here the boundary conditions $\psi(0) = 0$ and $\psi(L) = 0$, and therefore

$$\begin{aligned} b &= 0 \\ a \sin(kL) &= 0 \quad . \end{aligned}$$

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Therefore $k = \frac{n\pi}{L}$ has to hold for an integer **quantum number** n , characterizing the bound state.

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- The derivative of the wave function may show any discontinuity at $x = 0$ and $x = L$, since the potential is infinite there.

- Normalization of the wave function: Firstly must $\psi(x)$ be normalizable, which is here not a problem in the finite interval $[0, L]$. Secondly we can calculate the normalization constant a in dependence of the quantum number n :

$$\begin{aligned} 1 &= \langle \psi | \psi \rangle = \int_{-\infty}^{\infty} dx |\psi(x)|^2 \\ &= |a|^2 \int_0^L dx \sin^2\left(\frac{n\pi}{L}x\right) \\ &= |a|^2 \frac{L}{n\pi} \int_0^{n\pi} dy \sin^2 y \quad \text{mit } y = \frac{n\pi}{L}x \\ &= |a|^2 \frac{L}{n\pi} \frac{n\pi}{2} = |a|^2 \frac{L}{2}. \end{aligned}$$

Therefore $|a|^2 = \frac{2}{L}$, with any arbitrary phase for a , which we choose to be real-valued.

In total we obtain the

Solution for a particle in the infinite potential well

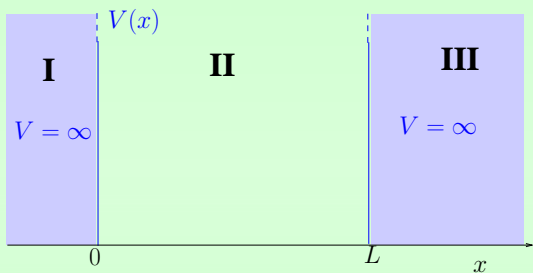
$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin(k_n x) , \quad 0 < x < L ; \quad (\psi(x) = 0 \text{ sonst}) \quad (7.7)$$

$$k_n = \frac{n\pi}{L} \quad ; \quad n = 1, 2, \dots \quad (7.8)$$

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 + V_0 \quad (7.9)$$

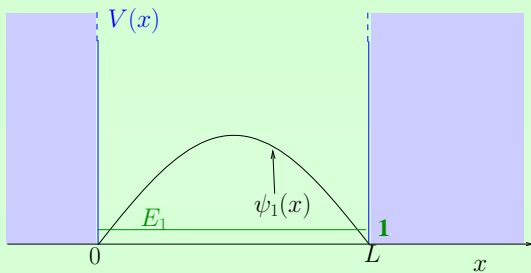
Therefore is here energy and wave number quantized, only allowing discrete possible values depending on the quantum number n . The energy increases with n^2 and decreases with $1/L^2$.

Figure 3 shows the wave functions for the three lowest eigenvalues. For each excitation the wave function crosses zero once more (so-called „nodes“).



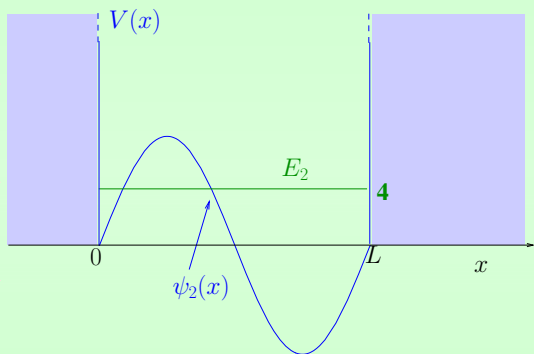
The four lowest eigenvalues with wave functions

Figure 3 shows the wave functions for the three lowest eigenvalues. For each excitation the wave function crosses zero once more (so-called „nodes“).



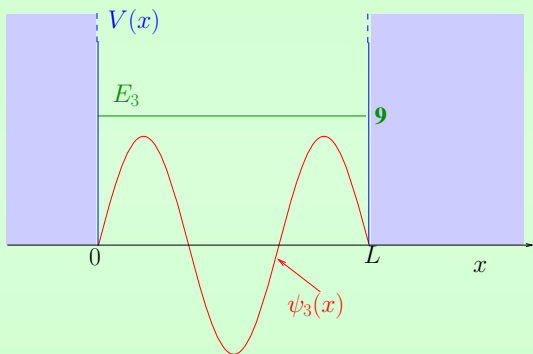
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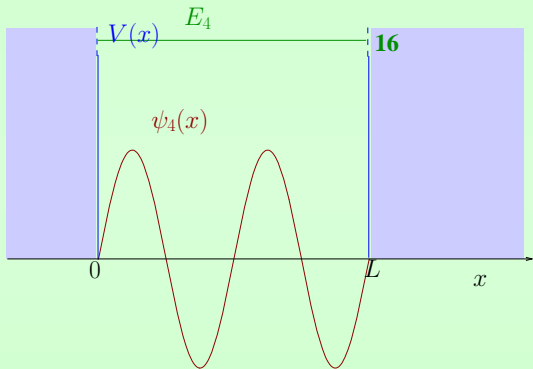
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The four lowest eigenvalues with wave functions

examples:

Force transmission to the walls

The force can be calculated from the energy


$$\begin{aligned} F &= -\frac{dE}{dL} \\ &= \frac{\hbar^2 \pi^2 n^2}{2m} \cdot \frac{2}{L^3} = \frac{\hbar^2 \pi^2 n^2}{mL^3} . \end{aligned}$$

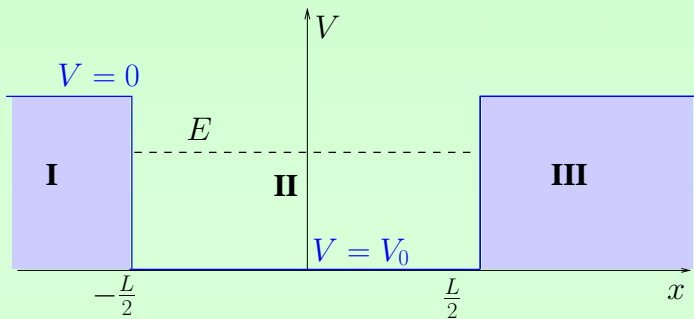
The energy of a state is lower in a broader well, due to this a force acts on the wall, trying to push them apart!

Finite potential well

Let's now assume a potential well of finite depth

$$V(x) = \begin{cases} V_0 & \text{for } |x| \leq L/2 \\ 0 & \text{otherwise} \end{cases} \quad ; V_0 < 0 \quad , \quad (7.10)$$

as shown in figure .



Finite potential well.

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The general solution

$$\psi(x) = A_1 e^{-qx} + A_2 e^{+qx} \quad (7.11)$$

$$\text{with} \quad q = \sqrt{\frac{2m|E|}{\hbar^2}} \quad (7.12)$$

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with different coefficients $A_{1,2}$ in the areas I and III.

In area I must be $A_1^I = 0$, For the same reason is $A_2^{III} = 0$ in area III.

In area II

4

$$\psi''(x) = -\frac{2m(|V_0| - |E|)}{\hbar^2} \psi(x) \quad .$$

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$$\text{with} \quad k = \sqrt{\frac{2m(|V_0| - |E|)}{\hbar^2}} \quad (7.14)$$

The entire wave function is therefore

$$\psi(x) = \begin{cases} A_1 e^{qx} & ; x < -\frac{L}{2} \\ B_1 e^{ikx} + B_2 e^{-ikx} & ; -\frac{L}{2} \leq x \leq \frac{L}{2} \\ A_2 e^{-qx} & ; x > \frac{L}{2} \end{cases} . \quad (7.15)$$

The coefficients can be calculated from the continuity conditions of the function and its derivatives.

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either symmetric or antisymmetric under $x \rightarrow -x$:

$$\text{symmetric} \quad \psi_s(x) = \begin{cases} A_s e^{qx} & ; x \leq -\frac{L}{2} \\ B_s \cos(kx) & ; -\frac{L}{2} \leq x \leq \frac{L}{2} \\ A_s e^{-qx} & ; x \geq \frac{L}{2} \end{cases} \quad (7.16a)$$

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$$\text{anti-symmetric} \quad \psi_a(x) = \begin{cases} A_a e^{qx} & ; x \leq -\frac{L}{2} \\ B_a \sin(kx) & ; -\frac{L}{2} \leq x \leq \frac{L}{2} \\ -A_a e^{-qx} & ; x \geq \frac{L}{2} \end{cases} \quad (7.16b)$$

We start with the **symmetric case**
continuity conditions:

$$\left. \begin{aligned} \psi_s\left(\frac{L}{2}\right) : \quad A_s e^{-q\left(\frac{L}{2}\right)} &= B_s \cos(kL/2) \\ \psi'_s\left(\frac{L}{2}\right) : \quad -A_s e^{-q\left(\frac{L}{2}\right)} &= -\frac{k}{q} B_s \sin(kL/2) \end{aligned} \right\}$$

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The left side is a **homogeneous** system of linear equations for the coefficients A_s and B_s .

This system has only a non-trivial solution, when the determinant vanishes. Since q and k depend on E (compare [7.12](#) and [7.14](#)), it represents a condition for the energy.

This equations provides the **quantization condition** for the allowed energy eigenvalues (in the symmetric case).

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Here we have defined: $\tilde{V}_0 \equiv \left(\frac{L}{2}\right)^2 \frac{2m}{\hbar^2} |V_0|$.

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This yields a relation between k and q :

$$\frac{q}{k} = \frac{\sqrt{\tilde{V}_0 - \eta^2}}{\eta} \tag{7.18}$$

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$$\frac{q}{k} = \frac{\sqrt{\tilde{V}_0 - \eta^2}}{\eta} \quad (7.18)$$

The condition equation 7.17 therefore results **for the symmetric case** to

$$\tan(\eta) = \frac{q}{k} = \frac{\sqrt{\tilde{V}_0 - \eta^2}}{\eta} \quad (7.19)$$

The **antisymmetric case** behaves identically. The calculation steps are here presented without further explanation.

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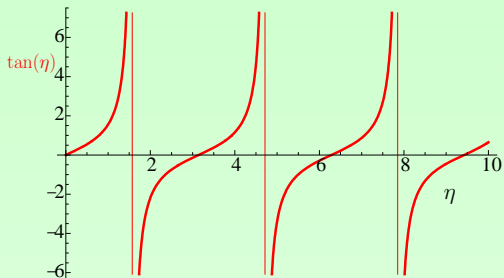
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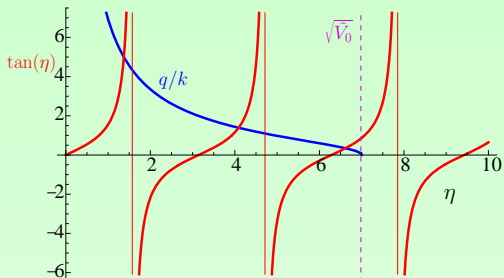
7.18 holds also in the **antisymmetric case**, so that:

$$\tan(\eta) = -\frac{k}{q} = -\frac{\eta}{\sqrt{\tilde{V}_0 - \eta^2}} \quad (7.21)$$

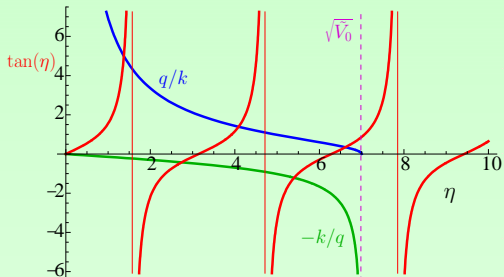


We can obtain the graphical solution of the implicit equations for η 7.19 and 7.21 from the intersection points of the curve $\tan(\eta)$ shown in figure

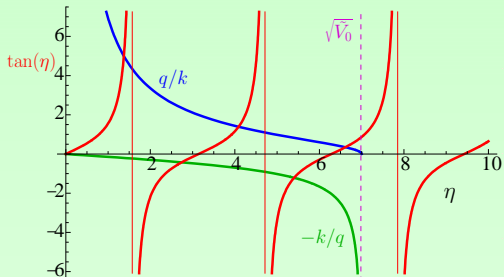
5



We can obtain the graphical solution of the implicit equations for η [7.19](#) and [7.21](#) from the intersection points of the curve $\tan(\eta)$ shown in figure [5](#) with the curves q/k

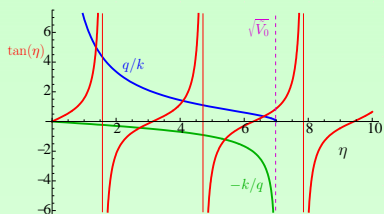


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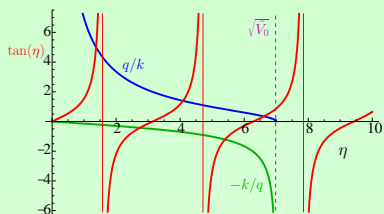


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One can see, that independently from \tilde{V}_0 there is always an intersection with the q/k -curve. This means there is always at least one symmetric, bound state.

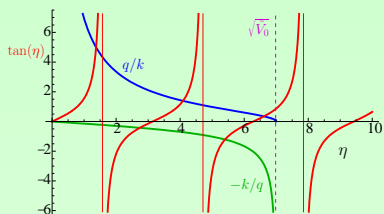


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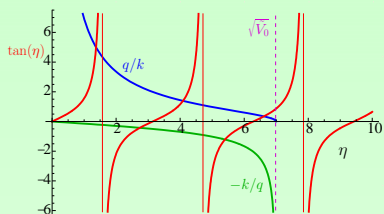
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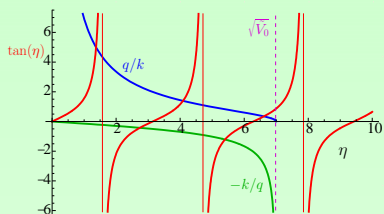


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The number of anti-symmetric eigenvalues is given by $\text{int}(\frac{\sqrt{\tilde{V}_0}}{\pi} + 1/2)$ (Exercises).

For the final determination of the wave function we use the continuity conditions [7.17](#) and [7.20](#)

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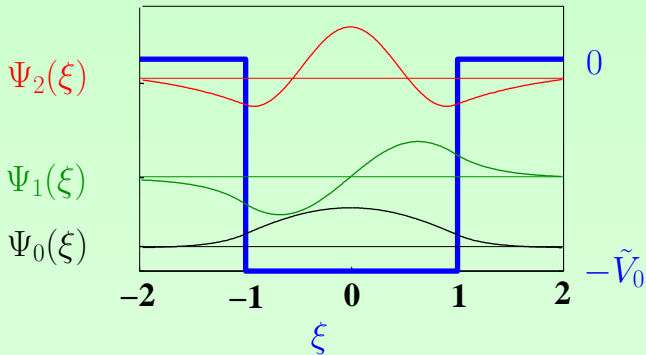
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and obtain with the dimensionless length $\xi = x/(L/2)$

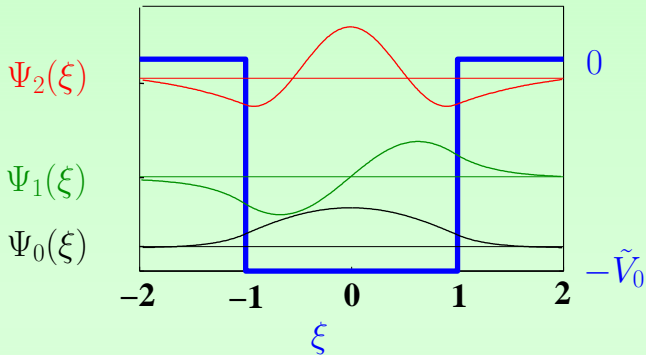
$$\Psi_s(\xi) = B_s \begin{cases} \cos(\eta) e^{q(\xi+1)} & , \xi < -1 \\ \cos(\eta\xi) & , -1 \leq \xi \leq +1 \\ \cos(\eta) e^{-q(\xi-1)} & , \xi > +1 \end{cases} \quad (7.22a)$$

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The parameters $B_{a/s}$ come from the normalization. It is not imperative to normalize the wave function, however, one has to take this into account when calculating expectation values, probabilities, etc.

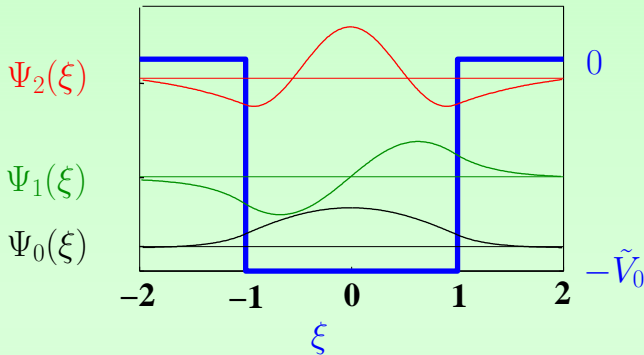


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With increasing n , the wave function protrudes outside of the potential well.

Summary: bound states

From the results obtained above for the special (box-shaped) potentials, we try to derive more general results for bound states in one dimension without proof. For this we take a look at continuous potentials $V(x)$, for which $\lim_{x \rightarrow \pm\infty} V(x) = V_\infty < \infty$, where we can choose without restriction $V_\infty = 0$. Furthermore, we take $V(x) \leq 0$.

Summary: bound states

- bound states have negative energy eigenvalues.³

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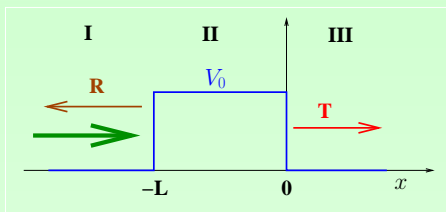
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- in one dimension there is always at least one bound state

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Scattering at a potential barrier



We will now quantum mechanically investigate the **scattering process** of particles at a potential. Next, we will focus on **unbound states**. **reflection coefficient** and **transmission coefficient**, respectively.

$$R = \frac{\text{number of reflected particles}}{\text{number of incoming particles}}$$

$$T = \frac{\text{number of transmitted particles}}{\text{number of incoming particles}}$$

In the **classical case**, the situation is simple:
if $E > V_0$, the particle can pass through the potential (it is only slowed down during the process of passing), therefore $T = 1, R = 0$,
while in the case that $E < V_0$ it will certainly be completely reflected,
therefore $T = 0, R = 1$.

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Behind the barrier (domain III) $A_2 = 0$ in this domain.

In the domain II 7 is

$$\psi(x) = B_1 \cdot e^{qx} + B_2 \cdot e^{-qx}$$

with $q = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$ being real-valued and > 0 . (7.25)

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$$\psi(x) = \begin{cases} A_1 e^{ikx} + A_2 e^{-ikx} & ; x \leq -L \\ B_1 e^{qx} + B_2 e^{-qx} & ; -L \leq x \leq 0 \\ C e^{ikx} & ; x \geq 0 \end{cases} .$$

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The continuity conditions of $\psi(x)$ and $\psi'(x)$ give 4 boundary conditions to determine 5 unknown coefficients A_1, A_2, B_1, B_2, C .⁴

⁴We can already see a difference to the case of bound states, where the number of unknown coefficients was equal to the number of conditions. 

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As said before, we are interested in the reflection and transmission coefficients

$$R = \left| \frac{n_r}{n_e} \right| = \frac{|A_2|^2}{|A_1|^2} = |A_2|^2$$
$$T = \left| \frac{n_t}{n_e} \right| = \frac{|C|^2}{|A_1|^2} = |C|^2 \quad ,$$

where n_e, n_r, n_t denote the (probability) densities of the incoming, reflected and transmitted particles.

This results in

$$\psi(x) = \begin{cases} e^{ikx} + A e^{-ikx} & ; x \leq -L \\ B_1 e^{qx} + B_2 e^{-qx} & ; -L \leq x \leq 0 \\ C e^{ikx} & ; x \geq 0 \end{cases} . \quad (7.26)$$

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One important consequence is therefore that:

For unbound states, the energies are not quantized, they form a continuum

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$$1 - \underbrace{|A|^2}_R = \underbrace{|C|^2}_T \quad (7.30)$$

Quantum tunnelling

We here want to investigate the interesting case $qL \gg 1$. This is the **quantum tunnelling regime**.

It describes the tunnelling process of a particle through a barrier, which is higher than the particle energy.

Applications: Scanning tunnelling microscope, Alpha-decay.

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From 7.29 we then obtain

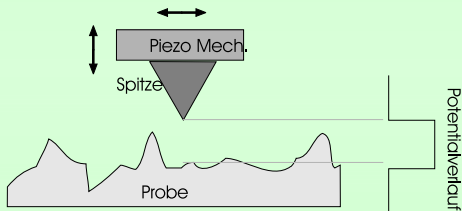
$$T = |C|^2 = \frac{16\rho^2}{(1 + \rho^2)^2} e^{-2qL}. \quad (7.31)$$

The coefficient of L in the exponent, $2q$ (inverse penetration depth), increases with the particle mass and with the difference between the energy and the barrier height (compare 7.25).

Application: Scanning tunnelling microscope

(Nobel-prize 1986 H.Rohrer, G.Binnig (IBM-Rüschlikon))

In a *Scanning Tunneling Microscope* (STM), a metal tip, controlled by a „piezo drive”, scans over a sample surface, compare figure 8.

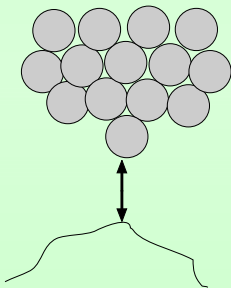


The conducting (or made conducting) sample is being scanned row by row. Between the tip and the sample is an electric potential, inducing a „tunnelling current” depending on the distance between the tip and the local sample surface.

With the help of the piezo setup, the metal tip can be kept oriented perpendicularly with respect to the sample surface, when scanning. There are different modes of operation on an STM. In one mode, the tip is rapidly readjusted to keep the tunnelling current constant. The therefore necessary shift of the tip is a measure for the height of the sample surface.

An STM has atomic resolution. At first, this seems unlikely, as the tip has macroscopic dimensions.

The reason why this method works, is, however, that due to the exponential dependence of the tunnelling current on the distance, the „lowermost atom” of the tip contributes the dominant part of the current (compare figure 9).



Tip of the scanning tunnelling microscope.

Resonance

A further important quantum effect is the **scattering resonance**.

This occurs at energies $E > V_0$, if the **barrier width is a multiple of the half wave length inside the barrier**, so that the wave „fits” inside the barrier.

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For $E > 0$, we can take over the results of the foregoing section (Eq. 7.27), with

$$q = i \bar{q} \quad \text{while} \quad \bar{q} \quad \text{being real-valued.} \quad (7.32)$$

The wave length inside the barrier is then $\frac{2\pi}{\bar{q}}$.

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For $E > 0$, we can take over the results of the foregoing section (Eq. 7.27), with

$$q = i \bar{q} \quad \text{while} \quad \bar{q} \quad \text{being real-valued.} \quad (7.32)$$

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One can derive this from 7.27, where $\bar{B}_1 = \pm B_1$ and $\bar{B}_2 = \pm B_2$,⁵ therefore

$$e^{-ikL} + Ae^{ikL} = \pm C = e^{-ikL} - Ae^{ikL} \Rightarrow A = 0 \Rightarrow R = 0, T = 1.$$

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For $E > V_0$ is $-i\rho = \frac{\bar{q}}{k} \rightarrow 1$ (compare 7.24, 7.25, 7.27, 7.32), so that $B_2 = 0$, $A = 0$, $B_1 = C = 1$, therefore $T = 1$.

Functions as Vectors

Wave functions of quantum mechanics belong to an infinite-dimensional vector space, the **Hilbert space**. In this section, we want to present an Heuristic treatment of functions in terms of vectors, skipping rigorous mathematical definitions.

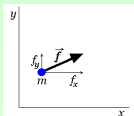
There are certain continuity and convergence restriction, which we are not going to discuss here.

A more rigorous treatment can be found in standad mathematics literature about Hilbert spaces.

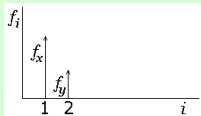
The main point here is that most results about vectors, scalar products, matrices, can be extended to linear vector spaces of functions.

This part is based largely on the Lecture Notes of L. van Dommelen. There are, however, some modifications.

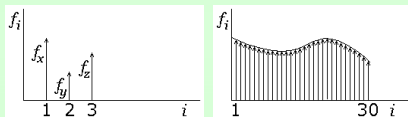
A vector \mathbf{f} (which might be velocity \mathbf{v} , linear momentum $\mathbf{p} = m\mathbf{v}$, force \mathbf{F} , or whatever) is usually shown in physics in the form of an arrow:



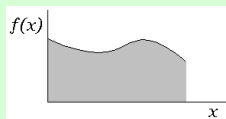
However, the same vector may instead be represented as a spike diagram, by plotting the value of the components versus the component index:



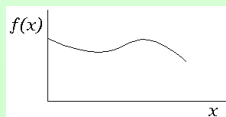
In the same way as in two dimensions, a vector in three dimensions, or, for that matter, in thirty dimensions, can be represented by a spike diagram:



For a large number of dimensions, and in particular in the limit of infinitely many dimensions, the large values of i can be rescaled into a continuous coordinate, call it x . For example, x might be defined as i divided by the number of dimensions. In any case, the spike diagram becomes a function $f(x)$:



The spikes are usually not shown:



In this way, a function is just a vector in infinitely many dimensions.

Key Points

- ◇ Functions can be thought of as vectors with infinitely many components.
- ◇ This allows quantum mechanics do the same things with functions as you can do with vectors.

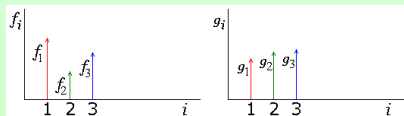
The scalar product

The scalar product makes it possible to find the length of a vector, by multiplying the vector by itself and taking the square root. It is also used to check if two vectors are orthogonal:

The usual scalar product of two vectors \mathbf{f} and \mathbf{g} can be found by multiplying components with the same index i together and summing that:

$$\mathbf{f} \cdot \mathbf{g} \equiv f_1g_1 + f_2g_2 + f_3g_3$$

Figure 10 shows multiplied components using equal colors.



Note the use of numeric subscripts, f_1 , f_2 , and f_3 rather than f_x , f_y , and f_z ; it means the same thing. Numeric subscripts allow the three term sum above to be written more compactly as:

$$\mathbf{f} \cdot \mathbf{g} \equiv \sum_{\text{all } i} f_i g_i$$

The length of a vector \mathbf{f} , indicated by $|\mathbf{f}|$ or simply by f , is normally computed as

$$|\mathbf{f}| = \sqrt{\mathbf{f} \cdot \mathbf{f}} = \sqrt{\sum_{\text{all } i} f_i^2}$$

However, this does not work correctly for complex vectors.

Therefore, it is necessary to use a generalized “scalar product” for complex vectors, which puts a complex conjugate on the first vector:

$$\langle \mathbf{f} | \mathbf{g} \rangle \equiv \sum_{\text{all } i} f_i^* g_i \quad (8.1)$$

The length of a nonzero vector is now always a positive number:

$$|\mathbf{f}| = \sqrt{\langle \mathbf{f} | \mathbf{f} \rangle} = \sqrt{\sum_{\text{all } i} |f_i|^2} \quad (8.2)$$

In 8.1 we have introduced the Dirac notation, which is quite common in quantum mechanics. Here, one takes the scalar product “bracket” verbally apart as

$$\langle \mathbf{f} | \quad | \mathbf{g} \rangle$$

bra \notin ket

and refer to vectors as bras and kets. This is useful in many aspects: it identifies which vector is taken as complex conjugate, and it will provide a elegant way to write operators. More details are given in Sec. 9.

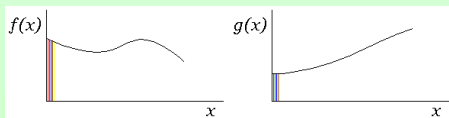
The scalar product of functions is defined in exactly the same way as for vectors, by multiplying values at the same x position together and summing. But since there are infinitely many (a continuum of) x -values, one multiplies by the distance Δx between these values:

$$\langle f|g \rangle \approx \sum_i f^*(x_i)g(x_i) \Delta x$$

which in the continuum limit $\Delta x \rightarrow 0$ becomes an integral:

$$\boxed{\langle f|g \rangle = \int_{\text{all } x} f^*(x)g(x) dx} \quad (8.3)$$

as illustrated in figure 11.



The equivalent of the length of a vector is in case of a function called its “norm:”

$$\|f\| \equiv \sqrt{\langle f|f \rangle} = \sqrt{\int |f(x)|^2 dx} \quad (8.4)$$

The double bars are used to avoid confusion with the absolute value of the function.

A vector or function is called “normalized” if its length or norm is one:

$$\langle f|f \rangle = 1 \text{ iff } f \text{ is normalized.} \quad (8.5)$$

Two vectors, or two functions, f and g are by definition orthogonal if their scalar product is zero:

$$\langle f|g \rangle = 0 \text{ iff } f \text{ and } g \text{ are orthogonal.} \quad (8.6)$$

Sets of vectors or functions that are all

- mutually orthogonal, and
- normalized

occur a lot in quantum mechanics. Such sets are called „orthonormal“. So, a set of functions or vectors f_1, f_2, f_3, \dots is orthonormal if

$$0 = \langle f_1|f_2 \rangle = \langle f_2|f_1 \rangle = \langle f_1|f_3 \rangle = \langle f_3|f_1 \rangle = \langle f_2|f_3 \rangle = \langle f_3|f_2 \rangle = \dots$$

and

$$1 = \langle f_1|f_1 \rangle = \langle f_2|f_2 \rangle = \langle f_3|f_3 \rangle = \dots$$

Key Points

- ◇ To take the scalar product of vectors, (1) take complex conjugates of the components of the first vector; (2) multiply corresponding components of the two vectors together; and (3) sum these products.
- ◇ To take an scalar product of functions, (1) take the complex conjugate of the first function; (2) multiply the two functions; and (3) integrate the product function. The real difference from vectors is integration instead of summation.
- ◇ To find the length of a vector, take the scalar product of the vector with itself, and then a square root.
- ◇ To find the norm of a function, take the scalar product of the function with itself, and then a square root.
- ◇ A pair of functions, or a pair of vectors, are orthogonal if their scalar product is zero.
- ◇ A set of functions, or a set of vectors, form an orthonormal set if every one is orthogonal to all the rest, and every one is of unit norm or length.

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Operators

This section defines linear operators (or, more simply operators), which are a generalization of matrices. Operators are the principal components of quantum mechanics.

In a finite number of dimensions, a matrix \hat{A} can transform any arbitrary vector \mathbf{v} into a different vector $\hat{A}\mathbf{v}$:

$$\mathbf{v} \xrightarrow{\text{matrix } \hat{A}} \mathbf{w} = \hat{A}\mathbf{v}$$

Similarly, an operator transforms a function into another function:

$$f(x) \xrightarrow{\text{operator } \hat{A}} g(x) = \hat{A}f(x)$$

Some simple examples of operators:

$$f(x) \xrightarrow{\hat{x}} g(x) = x f(x)$$

$$f(x) \xrightarrow{\frac{d}{dx}} g(x) = f'(x)$$

Note that a hat ($\hat{}$) is often used to indicate operators, and to distinguish them from numbers; for example, \hat{x} is the symbol for the operator that corresponds to multiplying by x . If it is clear that something is an operator, such as d/dx , no hat will be used.

It should really be noted that the operators we are interested in quantum mechanics are “linear” operators, i. e. such that for two functions \mathbf{f} and \mathbf{g} and two numbers a and b :

$$\hat{A} (a \mathbf{f} + b \mathbf{g}) = a \hat{A} \mathbf{f} + b \hat{A} \mathbf{g} \quad (8.7)$$

Key Points

- ◇ Matrices turn vectors into other vectors.
- ◇ Operators turn functions into other functions.

Eigenvalue Problems

To analyze quantum mechanical systems, it is normally necessary to find so-called eigenvalues and eigenvectors or eigenfunctions. This section defines what they are.

A nonzero vector \mathbf{v} is called an eigenvector of a matrix \hat{A} if $\hat{A}\mathbf{v}$ is a multiple of the same vector:

$$\hat{A}\mathbf{v} = a\mathbf{v} \text{ iff } \mathbf{v} \text{ is an eigenvector of } \hat{A} \quad (8.8)$$

The multiple a is called the eigenvalue. It is just a number.

A nonzero function \mathbf{f} is called an eigenfunction of an operator \hat{A} if $\hat{A}\mathbf{f}$ is a multiple of the same function:

$$\hat{A}\mathbf{f} = a\mathbf{f} \text{ iff } \mathbf{f} \text{ is an eigenfunction of } \hat{A}. \quad (8.9)$$

For example, e^x is an eigenfunction of the operator d/dx with eigenvalue 1, since $de^x/dx = 1e^x$.

However, eigenfunctions like e^x are not very common in quantum mechanics since they become very large at large x , and that typically does not describe physical situations. The eigenfunctions of d/dx that do appear a lot are of the form e^{ikx} , where $i = \sqrt{-1}$ and k is an arbitrary real number. The eigenvalue is ik :

$$\frac{d}{dx}e^{ikx} = ik e^{ikx}$$

Function e^{ikx} does not blow up at large x ; in particular, the Euler identity says:

$$e^{ikx} = \cos(kx) + i \sin(kx)$$

The constant k is called the wave number.

Key Points

- ◇ If a matrix turns a nonzero vector into a multiple of that vector, that vector is an eigenvector of the matrix, and the multiple is the eigenvalue.
- ◇ If an operator turns a nonzero function into a multiple of that function, that function is an eigenfunction of the operator, and the multiple is the eigenvalue.

Hermitian Operators

Most operators in quantum mechanics are of a special kind called “Hermitian”. This section lists their most important properties. The **Hermitian conjugate** \hat{A}^\dagger of an operator \hat{A} , corresponds, for finite-dimensional spaces to the transpose, complex conjugate of the matrix \hat{A} :

$$\hat{A}^\dagger = (\hat{A}^T)^* . \quad (8.10)$$

In general, for given \hat{A} it is defined as the operator for which

$$\langle f | \hat{A} g \rangle = \langle \hat{A}^\dagger f | g \rangle \quad (8.11)$$

for any vector $|f\rangle$ and $|g\rangle$.

An operator for which $\hat{A} = \hat{A}^\dagger$ is called **hermitian**. In other words, an hermitian operator can always be flipped over to the other side if it appears in a scalar product:

$$\langle f|\hat{A}g\rangle = \langle \hat{A}f|g\rangle \text{ always iff } \hat{A} \text{ is Hermitian.} \quad (8.12)$$

That is the definition, but Hermitian operators have the following additional special properties, which, again, are very similar to the corresponding properties of Hermitian matrices.

- They always have real eigenvalues. (But the eigenfunctions, or eigenvectors if the operator is a matrix, might be complex.) Physical values such as position, momentum, and energy are ordinary real numbers since they are eigenvalues of Hermitian operators (we will see this later).
- Their eigenfunctions can always be chosen so that they are normalized and mutually orthogonal, in other words, an orthonormal set.
- Their eigenfunctions form a “complete” set. This means that *any* function can be written as some linear combination of the eigenfunctions.

- In summary, the set $\{f_n(x)\}$ of eigenfunctions of an Hermitian operator can be chosen as **an orthonormal basis set** for the infinite-dimensional space. This is a very important property. It means that once we have found the infinite set of eigenfunctions $f_n(x)$ of an hermitian operator, we can write any $f(x)$ as

$$f(x) = \sum_n a_n f_n(x) \quad (8.13)$$

We will not discuss here issues of convergence.

An important issue, however, which is peculiar of function spaces, is the fact that the set of eigenvalues of an operator is not always discrete, but sometimes continuous. We will discuss this issue later.

- From now on, unless otherwise specified, when we refer to a **basis** we mean an **orthonormal (and of course complete) basis**.

The following properties of scalar products involving Hermitian operators are often needed, so they are listed here:

$$\text{If } \hat{A} \text{ is Hermitian: } \langle g|\hat{A}f\rangle = \langle f|\hat{A}g\rangle^*, \quad \langle f|\hat{A}f\rangle \text{ is real.} \quad (8.14)$$

Key Points

- ◇ Hermitian operators can be flipped over to the other side in scalar products.
- ◇ Hermitian operators have only real eigenvalues.
- ◇ Hermitian operators have a complete set of orthonormal eigenfunctions (or eigenvectors) that can be used as a basis.

Additional independent variables

In many cases, the functions involved in an scalar product may depend on more than a single variable x . For example, they might depend on the position (x, y, z) in three dimensional space.

The rule to deal with that is to ensure that the scalar product integrations are over *all* independent variables. For example, in three spatial dimensions:

$$\langle f|g\rangle = \int_{\text{all } x} \int_{\text{all } y} \int_{\text{all } z} f^*(x, y, z)g(x, y, z) dx dy dz$$

Note that the time t is a somewhat different variable from the rest, and time is *not* included in the scalar product integrations.

Dirac notation

The advantage of the Dirac notation is that it provides a natural way to carry out the operation between vectors and operators discussed in section 8. As much as possible, it provides also a unambiguous way to distinguish whether an object is a vector (notation as in Sec. 9.1), an operator (with „hat“ or as in Sec. 9.3), or a scalar (all the rest).

Vectors

As explained in Sec. 8.1, in the Dirac notations, vectors are represented in “bra” and “ket”. Here, we illustrate some useful operations that can be carried out with this formalism. We can write, for example, two vectors as linear combinations of other ones:

$$|f\rangle = \sum_n f_n |e_n\rangle$$

$$|g\rangle = \sum_n g_n |e_n\rangle$$

where g_n, f_n are coefficients (numbers).

We now evaluate their scalar product:

$$\langle g|f\rangle = \left(\sum_m g_m |e_m\rangle \right)^\dagger \left(\sum_n f_n |e_n\rangle \right)$$

The \dagger operation changes a “bra” into a “ket” and makes the complex conjugate of coefficients, we thus get

$$\langle g|f\rangle = \sum_{m,n} g_m^* f_n \langle e_m|e_n\rangle, \quad (9.1)$$

If, for example, the set of the $|e_n\rangle$ are orthonormal, then

$$\langle e_m|e_n\rangle = \delta_{n,m} \quad (9.2)$$

and we finally obtain the known result

$$\langle g|f\rangle = \sum_m g_m^* f_m. \quad (9.3)$$

Rules for operations



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- Complex conjugation turns a „bra“ into a „ket“ and vice-versa.
- **New** For operators in the for 9.5 or 9.7 (see below) hermitian conjugation is obtained by complex conjugation of the coefficients and by „flipping“ the bra and ket:

$$\left(\sum a_i |v_i \rangle \langle u_i| \right)^\dagger = \sum a_i^* |u_i \rangle \langle v_i| \quad (9.4)$$

Operators



Operators transform vectors in other vectors. As for matrices, an operator \hat{A} is completely specified, by specifying its action to any vector of the vector space.

I. e., if we know the result of $\hat{A}|v\rangle$ for all $|v\rangle$ we know \hat{A} .

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As a further alternative, it is sufficient to know all “matrix elements” of the operator between two elements of a basis set. I. e., for example we need to know $\langle e_n|\hat{A}|e_m\rangle$ for all n, m .

An operator can be written as a sum of terms of the form

$$\hat{A} = \sum_i a_i |v_i\rangle\langle u_i|, \quad (9.5)$$

(notice, this is different from the scalar product [9.3](#)) where a_i are numbers, and $|v_i\rangle$, $\langle u_i|$ are ket and bra vectors.

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The application of \hat{A} to a vector $|f\rangle$ gives (see the rules 9.2):

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In particular, in terms of its matrix elements $A_{m,n}$ in a complete basis, an operator can be written as

$$\hat{A} = \sum_{n,m} A_{n,m} |e_n\rangle\langle e_m|. \quad (9.7)$$

Hermitian Operators

We have already seen in 8.11 the definition for the Hermitian conjugate \hat{A}^\dagger of an operator \hat{A} (see also 9.4).

An operator \hat{A} for which $\hat{A} = \hat{A}^\dagger$ is called hermitian.

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An operator \hat{A} for which $\hat{A} = \hat{A}^\dagger$ is called **hermitian**.

It is thus straightforward to see that an operator \hat{A} is hermitian iff (cf. 8.12 for any $|f\rangle, |g\rangle$)

$$\langle g|\hat{A}f\rangle = \langle \hat{A}g|f\rangle = (\langle f|\hat{A}g\rangle)^* \quad (9.8)$$

where we have used one of the rules 9.2.

Hermitian Operators

We have already seen in [8.11](#) the definition for the **Hermitian conjugate** \hat{A}^\dagger of an operator \hat{A} (see also [9.4](#)).

An operator \hat{A} for which $\hat{A} = \hat{A}^\dagger$ is called **hermitian**.

It is thus straightforward to see that an operator \hat{A} is hermitian iff (cf. [8.12](#) for any $|f\rangle, |g\rangle$)

$$\langle g|\hat{A}f\rangle = \langle \hat{A}g|f\rangle = (\langle f|\hat{A}g\rangle)^* \quad (9.8)$$

where we have used one of the rules [9.2](#).

Using the expansion [9.7](#), we have

$$\sum_{n,m} A_{n,m} \langle g|e_n\rangle \langle e_m|f\rangle = \left(\sum_{n,m} A_{m,n} \langle f|e_m\rangle \langle e_n|g\rangle \right)^* = \sum_{n,m} A_{m,n}^* \langle g|e_n\rangle \langle e_m|f\rangle .$$

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Since this is valid for arbitrary $|g\rangle, |f\rangle$, we have

$$A_{m,n}^* = A_{n,m} \quad (9.9)$$

which for a finite-dimensional space corresponds to the relation (cf. [8.10](#)) for an hermitian matrix $A = (A^T)^*$. [examples:](#)

If \hat{A} is hermitian, it has a complete set of (orthonormal) eigenvectors $|a_n\rangle$ with eigenvalues a_n . In terms of this **basis set**,

$$\hat{A} = \sum_n a_n |a_n\rangle \langle a_n|, \quad (9.10)$$

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This can be easily verified by applying \hat{A} to one of its eigenvectors:

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Important is the **projection operator** on a (normalized) vector $|v\rangle$:

$$\hat{P}_v \equiv |v\rangle \langle v| \quad (9.11)$$

Continuous vector spaces

The space of quantum mechanical wave function can also contain **non-normalizable vectors**. An example is given by the wave functions of free particles (we discuss here for simplicity the one-dimensional case):

$$\phi_k(x) = \frac{e^{i k x}}{\sqrt{2\pi}}, \quad (9.12)$$

where the $\sqrt{2\pi}$ is taken for convenience. We denote by $|\tilde{k}\rangle$ the corresponding vector.

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where the $\sqrt{2\pi}$ is taken for convenience. We denote by $|\tilde{k}\rangle$ the corresponding vector.

These functions are **eigenfunctions of the momentum operator** $\hat{p} \equiv -i\hbar\frac{\partial}{\partial x}$ with eigenvalue $\hbar k$:

$$-i\hbar\frac{\partial}{\partial x}\phi_k(x) = \hbar k\phi_k(x) \iff \hat{p}|\tilde{k}\rangle = \hbar k|\tilde{k}\rangle \quad (9.13)$$

The scalar product between two of these functions is see:

$$\langle \tilde{k}' | \tilde{k} \rangle = \frac{1}{2\pi} \int e^{i(k-k')x} dx = \delta(k - k') . \quad (9.14)$$

So for $k = k'$ it is virtually “infinite”.

Physically this is because a wave function like 9.12 is homogeneously distributed in the whole space, so its normalized probability density should be zero everywhere! In other words, these functions are **not square integrable** ($\notin L^2$)

Of course these state vectors don't exist in reality. (The same holds for plane waves in electrodynamics). A physical state is a wave packet. However, it is mathematically useful to introduce them.

For practical purposes, one can extend the discussion of the previous part to such „non-normalizable vectors“ by using following modifications (we will prove this later)

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Of course, we must now find another name for these „non normalizable“ vectors. Since their index (here \tilde{k}) must be continuous, we will call them „continuum vectors“ as opposed to „discrete vectors“ (the former „normalizable“).

As for the case of discrete state vectors, we are interested in **eigenstates of hermitian operators**, for example the Hamiltonian \hat{H} :

$$\hat{H} |e(q)\rangle = e(q) |e(q)\rangle \quad (9.16)$$

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- their eigenfunctions constitute a complete basis set, i.e. any function can be expressed as a linear combination of such eigenfunctions.

Concerning the last point one should notice that in general an hermitian operator can admit both discrete as well as continuum eigenvectors.

Therefore, the expansion of a generic vector of the Hilbert space can contain contributions from both discrete as well as continuum basis vectors:

$$|f\rangle = \sum_n f_n |e_n\rangle + \int f(q) |e(q)\rangle d q \quad (9.17)$$

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An example is the Hamiltonian of the potential well with finite walls **7.10**: for $E < 0$ the eigenstates are discrete (bound states) and for $E > 0$ they are continuous (scattering states).

Real space basis

An important **continuum basis set** is provided by the **eigenfunctions of the position operator \hat{x}** , defined as

$$\hat{x} f(x) = x f(x) . \quad (9.19)$$

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These eigenfunctions are normalized according to the r.h.s. of **9.18**.

$$\langle x_0 | x_1 \rangle = \int \delta(x - x_0)^* \delta(x - x_1) d x = \delta(x_0 - x_1) . \quad (9.20)$$

here, $|x_0\rangle$ is the Dirac notation for the vector associated with $\delta(x - x_0)$.

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Notice that, given a vector $|f\rangle$, its scalar product with $|x_0\rangle$ is

$$\langle x_0 | f \rangle = \int \delta(x - x_0) f(x) dx = f(x_0) , \quad (9.21)$$

Change of basis and momentum representation

Expand an arbitrary vector $|f\rangle$ in the real-space basis $\{|x\rangle\}$ (cf. 9.17).

$$|f\rangle = \int c_x |x\rangle dx , \quad (9.22)$$

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From linear algebra, we know how to obtain the expansion coefficients c_x : we have to multiply from left by each element of the basis:

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Comparing with 9.21, we see that the expansion coefficients in the real-space basis are nothing else than the function associated with the vector $|f\rangle$ itself: $c_x = f(x)$.

By the way, the fact that each vector of the Hilbert space can be expanded as in 9.22, proves that the set of the $|x_0\rangle$ is indeed **complete**.

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$$|f\rangle = \int f_k |\tilde{k}\rangle dk \quad (9.23)$$

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$$|f\rangle = \int f_k |\tilde{k}\rangle dk \quad (9.23)$$

The coefficients f_k of the expansion are obtained as usual by „multiplying from left“, and using the continuum version of 9.3 as well as 9.12:

$$f_k = \langle \tilde{k} | f \rangle = \frac{1}{\sqrt{2\pi}} \int e^{-ikx} f(x) dx \equiv \tilde{f}(k) , \quad (9.24)$$

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i. e. the coefficients f_k are the Fourier transform $\tilde{f}(k)$ of $f(x)$. The function $\tilde{f}(k)$ represented in the „momentum“ basis is called the **momentum representation** of the vector $|f\rangle$.

Identity operator

We can adopt an useful expression for the **identity operator** \hat{I} in terms of a **complete, orthonormal basis** $\{|e_n\rangle\}$

$$\hat{I} = \sum_n |e_n\rangle\langle e_n|. \quad (9.25)$$

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this can be shown by observing that the operator relation 9.25 holds whenever applied to an arbitrary element $|e_m\rangle$ of the basis:

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Obviously, 9.25 must be suitably modified with the rules above, for the case in which all or part of the $|e_n\rangle$ are continuous.

We now use the same as [9.25](#) but for the real space basis.

$$\hat{I} = \int |x\rangle\langle x| dx \quad (9.26)$$

in order to reobtain [9.24](#) in an elegant way

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which, using $\langle x | \tilde{k} \rangle = \frac{1}{\sqrt{2\pi}} e^{ikx}$ (cf. [9.12](#)) gives the last term in [9.24](#).

[proof of the rules for continuum vectors:](#) : [Some applications:](#)

Principles and Postulates of Quantum Mechanics



The „postulates“ of quantum mechanics consist in part of a summary and a formal generalisation of the ideas which we have met up to now, in the course of the years they have been put together in order to understand the meaning and to provide a description for the puzzling physical results that had been observed.

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These postulates have been so far been confirmed by all experiments build up in order to verify (or falsify) their validity.

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These postulates have been so far been confirmed by all experiments build up in order to verify (or falsify) their validity.

Here, we will present these postulates together with practical examples. In these examples you will find again most of the concept introduced in the previous chapters.

Postulate I: Wavefunction or state vector

The state of a system is completely defined by a (time-dependent) vector $|\psi\rangle$ (state vector) of a Hilbert space.

⁶this is very interesting for quantum computers!

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For a given state $|\psi\rangle$ and an arbitrary c-number c , $c|\psi\rangle$ describes the same state as $|\psi\rangle$.

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Postulate II: Observables

Dynamical variables, so-called **observables**, i. e. properties that can be observed, measured, are represented by **Hermitian operators**

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Important examples of observables are:

- Coordinates: $\hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z})$
- Momentum: $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$, $\hat{p}_y = \dots$, \hat{p}_z ($\hat{\mathbf{p}} = -i\hbar\nabla$)
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Further observables are obtained from compositions (products and sums) of these
- Energy (**Hamiltonian or Hamilton operator**): $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$.
- Angular momentum $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$

Postulate III: Measure of observables

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A new concept is that **when measuring an observable, the only possible values that one can obtain are the eigenvalues** of the operator corresponding to the observable.

This means that not all classically allowed values of a physical quantity are allowed in quantum mechanics.

The most striking example is the **energy**: as we have seen, for bound states only **discrete** values of the energy are allowed.

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Even if one knows $|\psi\rangle$ with exact accuracy it is not possible (in general) to predict the outcome of the measure.

Possible results are statistically distributed, with a probability (density) that depends on $|\psi\rangle$. Details are given below.

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Here comes the big problem:

Even if one knows $|\psi\rangle$ with exact accuracy it is not possible (in general) to predict the outcome of the measure.

Possible results are statistically distributed, with a probability (density) that depends on $|\psi\rangle$. Details are given below.

The last important result (which again will be specified more in detail below) is:

A measure modifies the state vector:

After the measure of an observable, the particle falls into the eigenstate corresponding to the measured eigenvalue.

Measure of observables, more concretely

Let us illustrate the meaning of the measure postulate by using as an observable, the energy, associated with the hermitian operator \hat{H} (Hamiltonian).

The discussion below can be extended straightforwardly to any observable with discrete eigenvalues. The extension to continuous eigenvalues is also discussed.

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We, thus, denote by $|e_n\rangle$ the corresponding eigenvectors, i. e.

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$$e_n(x) = \langle x|e_n\rangle.$$

The eigenvalue condition is

$$\hat{H}|e_m\rangle = E_m|e_m\rangle. \quad (10.1)$$

Which tells us that a particle in the state $|e_n\rangle$ has the energy E_n .

However, an arbitrary physical state $|\psi\rangle$ can, in general consist of a linear combination of the $|e_n\rangle$:

$$|\psi\rangle = \sum_n a_n |e_n\rangle \quad (10.2)$$

Notice, first of all, that, once the basis is fixed, the state $|\psi\rangle$ is **completely specified by the coefficients a_n** . In a vector notation these are nothing else than the coordinates of the vector.

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The question is now, what the energy of this state is.

The way to answer this question is to **measure** the energy!

The crucial point, introduced above, is that

the outcome of the experiment cannot be foreseen,

even if one knows $|\psi\rangle$ exactly,

and even if one could carry out the experiment with arbitrary precision.

This unpredictability is **intrinsic** of quantum mechanics.

As discussed above, the measured energy will be one of the E_n .
The outcome is distributed statistically and the distribution is determined by $|\psi\rangle$.

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More precisely,:

The measure of the energy will give E_n with probability $W(E_n) \propto |a_n|^2$.

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More precisely,:

The measure of the energy will give E_n with probability $W(E_n) \propto |a_n|^2$.

The proportionality constant is given by the **normalisation condition**

$$\sum_n W(E_n) = 1.$$

This gives

$$W(E_n) = \frac{|a_n|^2}{\sum_m |a_m|^2} = \frac{|a_n|^2}{\langle\psi|\psi\rangle}. \quad (10.3)$$

Notice that for normalized states, the denominator in **10.3** is equal to 1 and can be dropped.

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This is the so-called **collapse of the wavefunction**. After the measure, the large amount of potential information contained in **10.2** (i.e. in its coefficients a_n) is lost, and only $a_{n_0} = 1$ remains !

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The striking aspect is that **a measure always disturbs the system**. This is in contrast to classical physics, where one could always think, at least in principle, to carry out a measure as little disturbing as possible, so that the state of the system is essentially not disturbed.

Continuous observables

Continuous observables

As we know, there are in general observables, such as the position \hat{x} , or the momentum \hat{p} operators, that admit **continuous eigenvalues**.

the discussion carried out for observables with discrete eigenvalues can be extended to ones with continuous eigenvalues upon **replacing probabilities with probability densities**.

see for a proof:

Reminder: probability density:

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For example, if we measure \hat{x} on the vector

$$|\psi\rangle = \int \psi(x)|x\rangle dx ,$$

then a measure of the position \hat{x} will give one of the possible x with **probability density** (cf. [10.3](#))

$$P(x) = \frac{|\psi(x)|^2}{\langle\psi|\psi\rangle} . \quad (10.4)$$

This is what we already learned in Sec. 6.

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After the measure, the state vector will collapse into the state $|x_0\rangle$, where x_0 is the value of x obtained in the measure.

Expectation values

A practical situation in physics is that one has many (a so-called ensemble of) particles all in the same state 10.2.

One can then repeat the measure of the energy for all these particles. The outcome being statistically distributed means that it will be, in general, different for each particle.

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If one knows the state, one can predict $\langle E \rangle$. As we show below, for the state 10.2 this is given by:

$$\langle E \rangle = \frac{\sum_n E_n |a_n|^2}{\sum_n |a_n|^2} = \frac{\langle \psi | \hat{H} \psi \rangle}{\langle \psi | \psi \rangle}, \quad (10.5)$$

where \hat{H} is the Hamilton operator, i. e. the operator associated with the energy observable.

The first equality in 10.5 is easily obtained by probability theory: the average value of E is given by the sum over all its possible values E_n weighted with their probability 10.3.

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To show the second equality, let us evaluate the numerator in the last term in 10.5:

$$\langle \psi | \hat{H} \psi \rangle = \sum_{n,m} a_n^* a_m \langle e_n | \underbrace{\hat{H} | e_m \rangle}_{E_m | e_m} \rangle =$$

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which corresponds to the numerator of the second term in 10.5.

Again, the above discussion holds for an arbitrary observable taken instead of the energy, provided one expands the quantum states in eigenstates of this observable, instead of the energy.

Continuous observables

For **continuous observables**, i. e. observables with a continuum of eigenvalues, such as \hat{x} , we adopt the usual rules and obtain, similarly to

10.5 :

$$\langle \hat{x} \rangle = \frac{\int x |\psi(x)|^2 dx}{\int |\psi(x)|^2 dx} = \frac{\langle \psi | \hat{x} \psi \rangle}{\langle \psi | \psi \rangle} . \quad (10.7)$$

Extension: standard deviation:

Example: Heisenberg uncertainty:

Example: qubits:

⋮

Postulate IV: Time evolution

We write 6.14 in terms of state vectors:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \quad (10.8)$$

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$$i\hbar \frac{\partial}{\partial t} a_n(t) |e_n\rangle = a_n(t) E_n |e_n\rangle . \quad (10.10)$$

We see that this reduces to a (well-known) differential equation for $a_n(t)$.

The solution was already found in 6.19:

$$a_n(t) = a_{n0} \exp\left(-i \frac{E_n t}{\hbar}\right) \quad (10.11)$$

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Eigenstates of \hat{H} are called **stationary states** because their time dependence is completely included in the time dependence of a multiplicative coefficient a_n , which, as we know, does not modify the state.

Generic state

The linearity of [10.8](#), as well as the above solution for an eigenstate of \hat{H} , immediately tells us the time dependence of an arbitrary state [10.2](#) written as a superposition of eigenstates of \hat{H} .

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$$|\psi(t)\rangle = \sum_n a_{n0} e^{-i\frac{E_n}{\hbar}t} |e_n\rangle \quad (10.12)$$

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Again, the above result also hold when the eigenvalues of the Hamilton operator are **continuous**.

example: free particle evolution:

Further examples

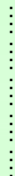
example: Qubits:

example: Tight-binding model:

Hydrogen atom:

Hydrogen atom excited states:

Momentum representation:



Examples and exercises



Wavelength of an electron

[back](#)

Determine the kinetic energy in eV for an electron with a wavelength of 0.5 nm (X-rays).

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$$\begin{aligned} & (6.6 \times 10^{-34} \text{ Js})^2 / (2(5 \times 10^{-10} \text{ m})^2 \times 9.1 \times 10^{-31} \text{ Kg}) \\ & = 9.6 \times 10^{-19} \text{ J} \times eV/eV = 9.6/1.6 \times 10^{-19+19} eV = 6eV \end{aligned}$$

Photoelectric effect

[back](#)

The work function of a particular metal is $2.6eV$
($1.eV = 1.6 \times 10^{-12} \text{ erg}$).

What maximum wavelength of light will be required to eject an electron from that metal?

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$$\frac{6.6 \times 10^{-34} \text{ Js} \times 3. \times 10^8 \text{ m/s}}{2.6 \times 1.6 \times 10^{-19} \text{ J}} \approx 4.8 \times 10^{-7} \text{ m} = 480 \text{ nm}$$

Some properties of a wavefunction

[back](#)

The ground-state wavefunction of the Hydrogen atom has the form

$$e^{-\frac{a}{2}r} \quad (11.1)$$

where $r = |\mathbf{r}|$ and $\mathbf{r} = (x, y, z)$.

Normalize the wavefunction.

Find the expectation value of the radius $\langle r \rangle$.

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Normalize the wavefunction.

Find the expectation value of the radius $\langle r \rangle$.

Find the probability $W(r_0 < r < r_0 + \Delta r_0)$ that r is found between r_0 and $r_0 + \Delta r_0$.

In the limit of small Δr_0 , the probability density $P(r_0)$ for r (not for \mathbf{r} !) is given by

$$P(r_0) \Delta r_0 = W(r_0 < r < r_0 + \Delta r_0) \quad (11.2)$$

Determine $P(r_0)$ and plot it.

Determine the most probable value of r (i. e. the maximum in $P(r_0)$).

Properties of a wavefunction

expectation values, normalisation, etc.

Normalisation:

$$1 = N^2 \int (e^{-\frac{a}{2}r})^2 dV = N^2 \int e^{-a r} dV \quad (11.3)$$

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The volume element in spherical coordinates (r, θ, ϕ) is given by $dV = r^2 dr \sin\theta d\theta d\phi$. The integral over the solid angle gives 4π .

We thus have:

$$1 = N^2 4\pi \int_0^\infty e^{-a r} r^2 dr = N^2 4\pi \frac{2}{a^3} \Rightarrow N = \sqrt{\frac{a^3}{8\pi}} \quad (11.4)$$

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Properties of a wavefunction

expectation values, normalisation, etc.

$W(r_0 < r < r_0 + \Delta r_0)$ is given by the integral 11.4 in between these limits:

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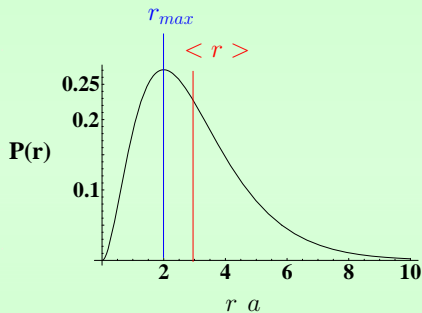
For small Δr_0 this is obviously given by the integrand times Δr_0 , so that

$$W(r_0 < r < r_0 + \Delta r_0) = P(r_0) \Delta r_0 = N^2 4 \pi e^{-a r_0} r_0^2 \Delta r_0 \quad (11.7)$$

The most probable value is given by the maximum of $P(r_0)$, this is easily found to be $r_{max} = \frac{2}{a}$.

Properties of a wavefunction

expectation values, normalisation, etc.



Notice that the probability density $P(\mathbf{r})$ for the **coordinates** $\mathbf{r} = (x, y, z)$ is given instead by $P(\mathbf{r}) = N^2 e^{-a r_0}$ and has its maximum at the centre $\mathbf{r} = 0$.

Particle in a box: expectation values



[back](#) Evaluate the expectation value $\langle x \rangle$ (average value) of the coordinate x for the ground state of the particle in a box. Evaluate its standard deviation $\Delta x \equiv \sqrt{\langle (x - \langle x \rangle)^2 \rangle}$.

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Solution:

Ground state

$$\psi(x) = N \sin \frac{\pi}{a} x \quad (11.8)$$

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Solution:

Ground state

$$\psi(x) = N \sin \frac{\pi}{a} x \quad (11.8)$$

Normalisation

$$1 = N^2 \int_0^a \left(\sin \frac{\pi}{a} x \right)^2 dx = N^2 \frac{a}{2} \Rightarrow N = \sqrt{\frac{2}{a}} \quad (11.9)$$

$$\langle x \rangle = \frac{2}{a} \int_0^a x \left(\sin \frac{\pi}{a} x \right)^2 dx = \frac{a}{2} \quad (11.10)$$

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$$\Delta x^2 = \langle x^2 \rangle - \langle x \rangle^2 = a^2 \left(\frac{1}{12} - \frac{1}{2\pi^2} \right) \quad (11.12)$$

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Delta-potential

Find the bound states and the corresponding energies for an attractive δ -potential

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$$\left. \begin{array}{l} \psi(x) = A e^{-qx} \quad x > 0 \\ \psi(x) = B e^{qx} \quad x < 0 \end{array} \right\} q = \sqrt{\frac{-2mE}{\hbar^2}}$$

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There is always one and only one bound state with energy $E = -\frac{u^2 m}{2\hbar^2}$

Delta-potential

Further exercises:

- Determine A so that the wave function is normalized
- Determine the unbound states and the transmission and reflection coefficients.

Expansion in a discrete (orthogonal) basis

[back](#)

The Hilbert space admits continuous, mixed (as in [9.17](#)), and also purely discrete (although infinite) basis sets. One example for the latter is provided by the eigenstates of the harmonic oscillator.

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- Write the expansion of two vectors $|f\rangle$ and $|g\rangle$ in a discrete basis $\{|b_n\rangle\}$, and express the scalar product $\langle g|f\rangle$ in terms of the expansion coefficients f_n and g_n .
(Of course, as expected the result is formally the same as in the finite-dimensional case [8.1](#)).

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(Of course, as expected the result is formally the same as in the finite-dimensional case [8.1](#)).
- Write an expansion of the function $f(x) \equiv \langle x|f\rangle$ in terms of the orthogonal functions $b_n(x) \equiv \langle x|b_n\rangle$. Write an expression for the expansion coefficients.

Solution:

Expansion:

$$|f\rangle = \sum_n f_n |b_n\rangle, \quad (11.13)$$

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The scalar product:

$$\langle g|f\rangle = \sum_{m,n} g_m^* f_n \underbrace{\langle b_m || b_n \rangle}_{\delta_{m,n}} = \sum_n g_n^* f_n,$$

cf. 8.1.

Expansion of $f(x)$: we multiply [11.13](#) from left with $\langle x|$:

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$$f_n = \langle b_n|f\rangle = \int \langle b_n|x\rangle \langle x|f\rangle dx = \int b_n(x)^* f(x) dx \quad (11.15)$$

Hermitian operators

[back](#)

Show that the momentum operator ($\hbar = 1$)

$$\hat{p} \equiv -i \frac{d}{dx}$$

is hermitian. Use the relation [8.12](#) and partial integration.

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Proof:

$$\langle g | \hat{p} f \rangle = \int g(x)^* \left(-i \frac{d}{dx} f(x) \right) dx = \int \left(-i \frac{d}{dx} g(x) \right)^* f(x) dx = \langle \hat{p} g | f \rangle$$

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$$\begin{aligned}\langle g | (\hat{A}\hat{B} + \hat{B}\hat{A}) f \rangle &= \langle g | \hat{A}\hat{B} f \rangle + \langle g | \hat{B}\hat{A} f \rangle = \\ &\langle \hat{A}g | \hat{B}f \rangle + \langle \hat{B}g | \hat{A}f \rangle = \langle \hat{B}\hat{A}g | f \rangle + \langle \hat{A}\hat{B}g | f \rangle = \\ &\langle (\hat{A}\hat{B} + \hat{B}\hat{A})g | f \rangle\end{aligned}$$

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[back](#)

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It is easy to see that this expression is valid for any other observable, including continuous ones.

Heisenberg's uncertainty

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Consider the wave function

$$\psi(x) = e^{-a x^2/2}$$

For large a the wave function is strongly peaked around $x = 0$, i. e. the uncertainty (standard deviation) Δx in the coordinate x is small.

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Here we want to illustrate the **Heisenberg uncertainty** principle, according to which a small uncertainty in x corresponds to a large uncertainty in the momentum p and vice-versa. To do this:

- Normalize ψ
- Evaluate $\langle \hat{x} \rangle$
- Evaluate $\Delta \hat{x}^2$
- Evaluate \hat{p}
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- Evaluate $\sqrt{\Delta \hat{p}^2} \sqrt{\Delta \hat{x}^2}$ and verify that it is independent of a

Heisenberg's uncertainty principle

Solution

$$\langle \psi | \psi \rangle = \int e^{-ax^2} dx = \sqrt{\pi/a} \implies \psi_N(x) \equiv (a/\pi)^{1/4} \psi(x) \text{ is normalized}$$

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Qubits and measure

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A qubit is described by two discrete states denoted by⁷ $|0\rangle$ and $|1\rangle$.

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- Determine the outcomes of the measures of B and N and their probabilities.
- Starting again with the ensemble prepared in $|0\rangle$, invert the order of the measures of N and B and determine outcomes and probabilities.

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Proof of hermiticity:

One way to show that the operators are Hermitian is to write them in matrix form (they are obviously 2×2 matrices):

$$\hat{B} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \quad \hat{N} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} . \quad (11.19)$$

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The other way is to use the rule [9.4](#). For \hat{B} it is straightforward, for \hat{N} :

$$\hat{N}^\dagger = (|1\rangle\langle 0| + |0\rangle\langle 1|)^\dagger = (|0\rangle\langle 1| + |1\rangle\langle 0|) = \hat{N}$$

Possible outcomes

The possible outcomes are given by the **eigenvalues** of the operators: \hat{B} has eigenvalues (and thus possible outcomes) $B = 0$ and $B = 1$ (it is the observable telling in which qubit the particle is). The eigenvectors are easily shown to be $|0\rangle$ and $|1\rangle$.

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However, for such a simple operator, it may be easier to solve the eigenvalue equation directly:

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By equating the coefficients of the two basis vectors we have

$$a = N b, \quad b = N a \Rightarrow N^2 = 1 \Rightarrow N = \pm 1. \quad (11.20)$$

For the second part of the problem it is useful to evaluate the eigenvectors, which we denote as $|N = -1\rangle$ and $|N = +1\rangle$ with obvious notation.

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$$|N = -1\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle) \quad |N = +1\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \quad (11.21)$$

Measure of (1) \hat{B} and (2) \hat{N}

Since the starting state $|0\rangle$ is already an eigenstate of \hat{B} , the expansion

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We now start from the ensemble of $|0\rangle$ and measure \hat{N} . This is the same situation as in the last measure of the previous case, since we had the same starting state.

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[11.21](#) is already the expansion of these states in eigenvalues of \hat{B} . We thus have that for the particles in $|N = -1\rangle$.

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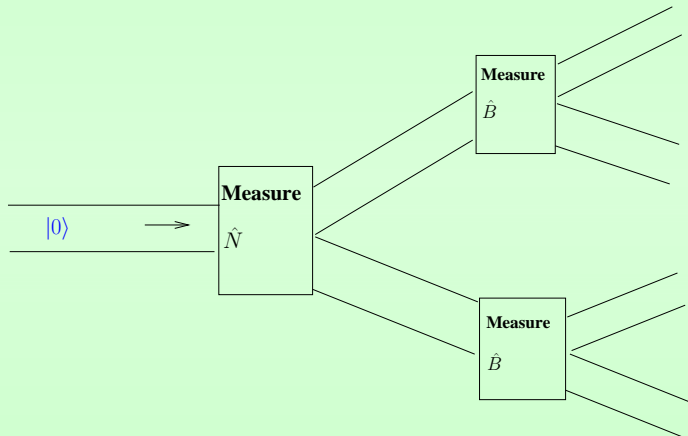
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The same result holds for the particles in $|N = +1\rangle$ so that [11.24](#) describes the global outcome of the second measure.

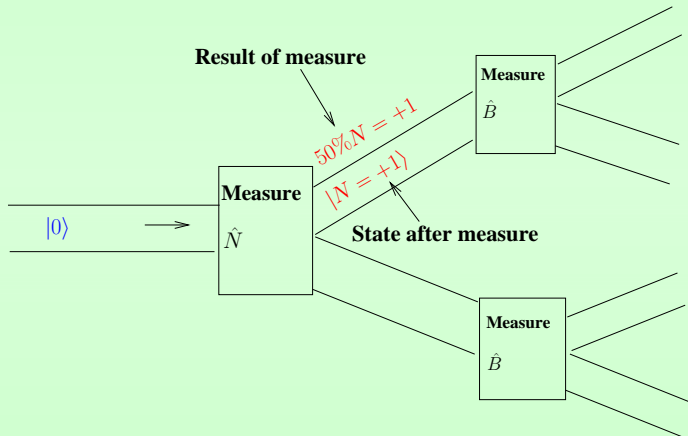
Schematic diagram of the processes

for the last measure sequence



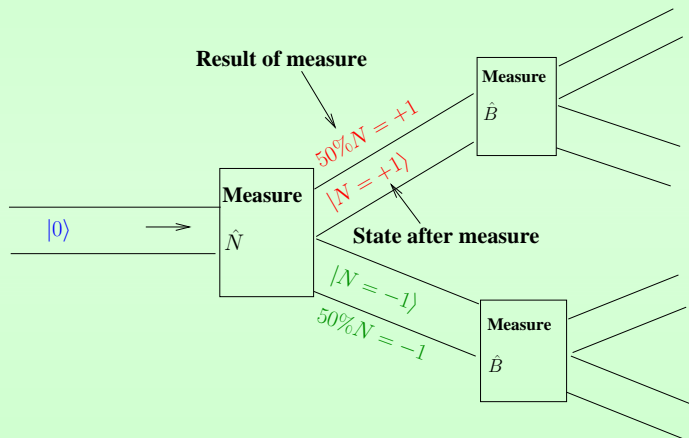
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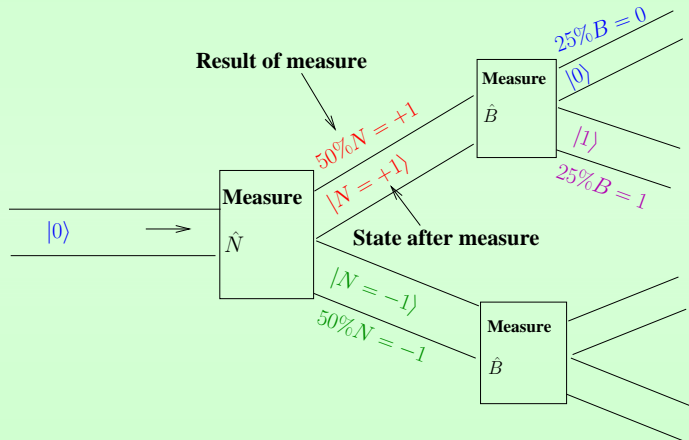
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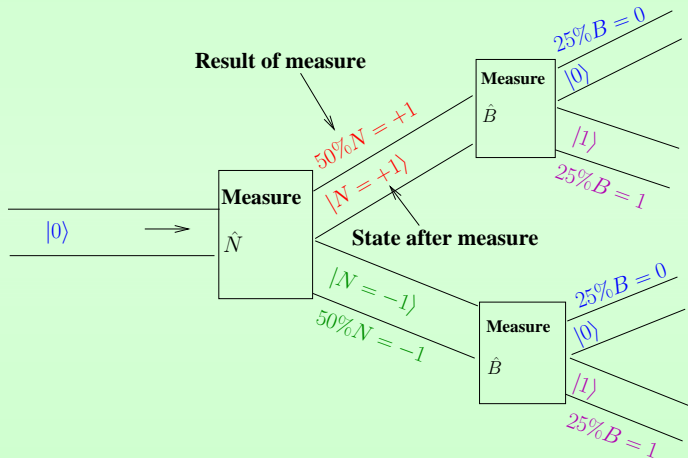
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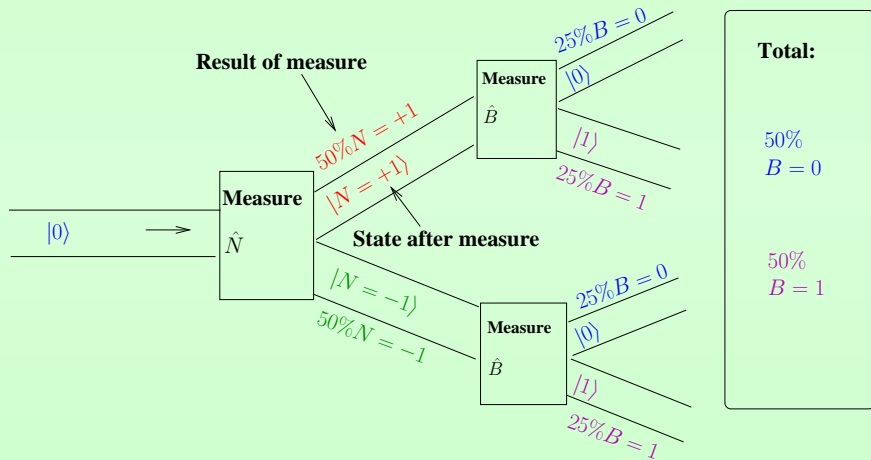
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- Measuring an observable changes the state of a quantum system (no matter how one tries to be „delicate“: the above results are **intrinsic**).
- When measuring different observables the possible outcomes depend, in general, upon the order of the measure.
- The example above applies, for example, to the (z -component of the) spin s_z (internal angular momentum) of an electron which can admit only two values $s_z = \pm \frac{\hbar}{2}$, corresponding to the two states $|0\rangle$ and $|1\rangle$. The observables B and N are then related to the z -component ($\hat{s}_z = \hbar(\hat{B} - \frac{1}{2})$) and the x -component ($\hat{s}_x = \frac{\hbar}{2}\hat{N}$) of the spin.

Qubits and time evolution

[back](#)

Consider the example on qubits above, take $\hbar = 1$.

At $t = 0$ a qubit is prepared in the state $|\psi(t = 0)\rangle = |0\rangle$.

The Hamiltonian of the system describes a particles hopping from one site to the other and is given by (see [11.18](#))

$$\hat{H} = a\hat{N} \quad (11.25)$$

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- Determine the expectation value $\langle \hat{N} \rangle$ and the square of the standard deviation $\langle (\Delta\hat{N})^2 \rangle$ versus t .
- Suppose one instead measures B at time t . Determine $P(B = 0)$, as well as $\langle \hat{B} \rangle$ and $\langle (\Delta\hat{B})^2 \rangle$ versus t .

Solution

According to 10.12, we must expand the initial state in eigenstates of the Hamiltonian. We have already done this in 11.22. From 10.12, the time evolution is given by ($\hbar = 1$)

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}(|N = -1\rangle e^{iat} + |N = +1\rangle e^{-iat}) \quad (11.26)$$

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From 10.3, and since the state is normalized, we have

$$P(N = +1) = \frac{1}{2}$$

independently of t .

Since, obviously, $P(N = -1) = 1 - P(N = +1)$, we have, again independent of t :

$$\langle \hat{N} \rangle = 1 P(N = +1) + (-1)P(N = -1) = 0$$

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There are several ways to do that. One is to first evaluate the operator

$$\begin{aligned} \hat{N}^2 &= (|1\rangle\langle 0| + |0\rangle\langle 1|)(|1\rangle\langle 0| + |0\rangle\langle 1|) = \\ &|1\rangle\langle 0||1\rangle\langle 0| + |1\rangle\langle 0||0\rangle\langle 1| + |0\rangle\langle 1||1\rangle\langle 0| + |0\rangle\langle 1||0\rangle\langle 1| = \end{aligned}$$

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Therefore $\langle N^2 \rangle = 1$, and we have (see 11.17):

$$\langle (\Delta \hat{N})^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = 1 \quad (11.27)$$

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For this we simply use the expressions 11.21, collect the coefficients of the basis vectors, and obtain:

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We thus have

$$P(B = 0) = (\cos at)^2 \quad P(B = 1) = (\sin at)^2$$

And thus

$$\langle \hat{B} \rangle = (\sin at)^2$$

We determine $\langle B^2 \rangle$ in a different way, namely by observing that eigenstates of \hat{B} are also eigenstates of \hat{B}^2 (this actually holds for any observable), and, in this case $B^2 = B$, so that $\langle \hat{B}^2 \rangle = \langle \hat{B} \rangle$, and

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$$\langle (\Delta \hat{B})^2 \rangle = \langle B^2 \rangle - \langle B \rangle^2 = (\sin at)^2 (1 - (\sin at)^2) = (\sin at)^2 (\cos at)^2 \quad (11.29)$$

Free-particle evolution

[back](#)

The wave function of a free particle ($V = 0$) at $t = 0$ is given by

$$\psi(x, t = 0) = e^{-ax^2/2}$$

determine the wave function $\psi(x, t)$ at time t .

Solution

According to 10.12 we have to expand $|\psi\rangle$ in eigenstate of the Hamiltonian $\hat{H} = \frac{p^2}{2m}$. These are also eigenstates of the momentum p , and are given in 9.12:

$$\phi_k(x) = \frac{e^{i k x}}{\sqrt{2\pi}}.$$

The expansion is given by (cf. 9.24)

$$|\psi\rangle = \int \langle \tilde{k} | \psi \rangle | \tilde{k} \rangle dk \quad (11.30)$$

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with

$$\langle \tilde{k} | \psi \rangle = \frac{1}{\sqrt{2\pi}} \int e^{-ikx} \psi(x) dx = e^{-\frac{k^2}{2a}} / \sqrt{a} \quad (11.31)$$

Following 10.12, the time evolution of 11.30 is given by

$$|\psi(t)\rangle = \int \langle \tilde{k} | \psi \rangle e^{-iE_k t/\hbar} |\tilde{k}\rangle dk$$

where the energy of the state $|\tilde{k}\rangle$ is

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Inserting [11.31](#) and again [9.12](#), we obtain

$$\psi(x, t) = \int \frac{e^{-\frac{k^2}{2a}}}{\sqrt{a}} e^{-i\hbar k^2 t / (2m)} \frac{1}{\sqrt{2\pi}} e^{-ikx} dk$$

Substituting $k = \sqrt{a}q$, and introducing the variable

$$T \equiv \frac{\hbar a t}{m}$$

we have

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int e^{-q^2 \frac{(1+iT)}{2} - iq\sqrt{a}x} dq$$

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The complicated integral gives finally

$$\psi(x, t) = \frac{e^{-\frac{ax^2}{2(1+iT)}}}{\sqrt{1+iT}}$$

The main effect is a broadening of the Gaussian function with time

$$\Delta x^2 \propto \frac{|1+iT|}{a}$$

Momentum representation of \hat{x}

[back](#)

Instead of the usual real-space representation,

$$|\psi\rangle = \int \psi(x)|x\rangle dx \quad \psi(x) = \langle x|\psi\rangle . \quad (11.32)$$

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a state vector can be written in the momentum representation (see [9.23](#)), i. e. expanded in eigenstates of momentum.

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In the real-space representation, we have learned that the action of the operators \hat{x} and \hat{p} correspond to the application of the operators x and $-i\hbar d/dx$ on the wave function $\psi(x)$ (we use $\hbar = 1$), respectively.

Show that in the momentum representation,

$$\hat{p}\tilde{\psi}(k) \rightarrow k\tilde{\psi}(k) \quad (11.34)$$

and

$$\hat{x}\tilde{\psi}(k) \rightarrow i\frac{d}{dk}\tilde{\psi}(k) \quad (11.35)$$

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now we compute the wavefunction of the vector $\hat{x}|\psi\rangle$:

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

The action of p is somewhat more complicated:

We compute the wavefunction of the vector $\hat{p}|\psi\rangle$. To obtain this we insert the identity

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$$\begin{aligned} \langle x|\hat{p}\psi\rangle &= \int \langle\hat{x}|\tilde{k}\rangle\langle\tilde{k}|\hat{p}\psi\rangle dk = \\ &= \int \frac{1}{\sqrt{2\pi}} e^{ikx} \langle\hat{p}\tilde{k}|\psi\rangle dk = \int k \frac{1}{\sqrt{2\pi}} e^{ikx} \tilde{\psi}(k) dk = \\ &= -i \frac{d}{dx} \int \frac{1}{\sqrt{2\pi}} e^{ikx} \tilde{\psi}(k) dk = -i \frac{d}{dx} \psi(x) \end{aligned}$$

where $\tilde{\psi}(k)$ is the Fourier transform of $\psi(x)$, see [9.24](#).

The action of p is somewhat more complicated:

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where $\tilde{\psi}(k)$ is the Fourier transform of $\psi(x)$, see [9.24](#).

Use a similar procedure to prove [11.34](#) and [11.35](#).

Start from

Solution:

$$\tilde{\psi}(k) = \langle \tilde{k} | \psi \rangle$$

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now compute the wavefunction in the momentum representation of the vector $\hat{p}|\psi\rangle$:

$$\langle \tilde{k} | \hat{p}\psi \rangle = \langle \hat{p}\tilde{k} | \psi \rangle = k \langle \tilde{k} | \psi \rangle = k\tilde{\psi}(k)$$

This proves the first result [11.34](#).

Compute the wavefunction in the momentum representation of the vector $\hat{x}|\psi\rangle$. To obtain this, insert the identity

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which proves the second result 11.35.

Ground state of the hydrogen atom

[back](#)

The Hamiltonian for the hydrogen atom is given by

$$\hat{H} = -\frac{\hbar^2 \nabla^2}{2m} + V(r) \quad (11.36)$$

$$V(r) = -\frac{\alpha}{r} \quad \alpha = \frac{e^2}{4\pi\epsilon_0} \quad (11.37)$$

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Remember that in polar coordinates

$$\nabla^2 \Psi = \frac{1}{r} \frac{\partial^2}{\partial r^2} r \Psi + \frac{1}{r^2} \nabla_{\theta, \phi}^2 \Psi = \frac{\partial^2}{\partial r^2} \Psi + \frac{2}{r} \frac{\partial}{\partial r} \Psi + \frac{1}{r^2} \nabla_{\theta, \phi}^2 \Psi, \quad (11.38)$$

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Look for a spherical symmetric solution of the form

$$\psi(r) = e^{-qr} \quad (11.39)$$

Find q and the corresponding eigenvalue

solution

$$\hat{H}\psi(r) = -\frac{\hbar^2}{2m} \frac{1}{r} (r\psi''(r) + 2\psi'(r)) - \frac{\alpha}{r}\psi(r) = -e^{-qr} \left(\frac{\hbar^2}{2m} (q^2 - \frac{2q}{r}) + \frac{\alpha}{r} \right) \stackrel{!}{=} Ee^{-qr}$$

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$$E = -E_{Ry} \equiv -\frac{\hbar^2}{2m} q^2 = -\frac{\alpha q}{2} \quad (11.41)$$

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Here, the characteristic decay length $a_0 \equiv q^{-1}$ is the Bohr radius, and $E_{Ry} \approx 13.6 \text{ eV}$ is the Rydberg energy, i. e. the ionisation energy of the hydrogen atom.

Excited isotropic states of the hydrogen atom

[back](#)

Using the same Hamiltonian as in the previous example [11.36](#).

Look for solutions of the form

$$\psi(r) = p(r) e^{-qr} \quad (11.42)$$

With $p(r)$ a polynomial in r , and $q > 0$.

To do this follow these steps:

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- For given q , fix the value of the energy E that solves the Schrödinger equation in the large- r limit.
(Hint: in the Schrödinger equation keep just leading terms for large r . Remember that if p is a polynomial in r , then $p'/p = O(1/r)$.)

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- Find the corresponding values of the energies.
- What happens when q does not belong to this set: what can one say about the large- r behavior of $\psi(r)$ in this case?

Solution

The Schrödinger equation [11.36](#) with [11.37](#) and [11.38](#) gives ($\hbar = 1$).

$$-2m\hat{H}\psi(r) = \psi''(r) + \frac{2}{r}\psi'(r) + \frac{2m\alpha}{r}\psi(r) = -2mE\psi(r)$$

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Using [11.42](#)

$$\begin{aligned} & (p''(r) - 2qp'(r) + q^2p(r))e^{-qr} + \frac{2}{r}(p'(r) - qp(r))e^{-qr} + \\ & \frac{2m\alpha}{r}p(r)e^{-qr} + 2mEp(r)e^{-qr} = 0 \end{aligned} \quad (11.43)$$

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The leading terms for large r are the ones with no derivatives of $p(r)$ and no r in the denominator:

$$(q^2p(r) + 2mEp(r))e^{-qr} \xrightarrow{r \rightarrow \infty} 0 \quad (11.44)$$

which gives

$$E = -\frac{q^2}{2m} \quad (11.45)$$

This is the same as 11.41 in the previous example, however, we have to fix q .

To this end we expand $p(r)$ explicitly

$$p(r) = \sum_{n=0}^N A_n r^n$$

and insert it into 11.43 along with the value of E above:

$$e^{-qr} \sum_{n=0}^N A_n \left[n(n-1)r^{n-2} - 2qnr^{n-1} + 2nr^{n-2} - 2qr^{n-1} + 2m\alpha r^{n-1} \right] = 0$$

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Collecting terms with the same power of r , we get

$$\sum_{n=0}^N r^n [A_{n+2} ((n+2)(n+1) + 2(n+2)) - 2A_{n+1} (q(n+1) + q - m\alpha)] = 0$$

Which gives the following recursion equation for the coefficients

$$A_{n+2} = 2A_{n+1} \frac{q(n+2) - m\alpha}{(n+2)(n+3)}$$

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In order for $p(r)$ to be a polynomial, the left-hand side must vanish at some finite, integer n . This gives

$$q = q_n = \frac{m\alpha}{\bar{n}} \quad \bar{n} = n + 2$$

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In principle $n = 0, 1, 2, \dots$, but, in fact, one can check that also $n = -1$ gives a solution (which corresponds to the one of the previous example 11.40). Therefore, $\bar{n} = 1, 2, 3, \dots$.

The (binding) energies 11.45, are given by

$$E = -\frac{q^2}{2m} = -E_{Ry} \frac{1}{\bar{n}^2} \quad \bar{n} = 1, 2, 3, \dots, \quad (11.46)$$

where E_{Ry} is given below 11.41. The behavior $\frac{1}{\bar{n}^2}$ is characteristics of the binding energies of the Hydrogen atom.

For q different from any q_n , we have

$$\frac{A_{n+2}}{A_{n+1}} \stackrel{n \rightarrow \infty}{\approx} \frac{2q}{n} \quad A_n \approx \text{const.} \frac{(2q)^n}{n!}$$

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$$p(r)e^{-qr} \approx \text{const.} \quad e^{2qr}e^{-qr} \approx \text{const.} \quad e^{qr}$$

i. e., the wave function diverges exponentially at $r \rightarrow \infty$. This, by the way, corresponds to negative q solution of the asymptotic equation 11.44.

Tight-binding model

[back](#)

This is a very simple model for the dynamic of an electron in a solid. We consider a circular chain consisting of L lattice points (L even) labeled by $n = 0, L - 1$. In each lattice point there is a single „orbital“. A particle on this orbital is described by the vector $|n\rangle$.

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$$\langle n|m\rangle = \delta_{n,m}$$

The Hamiltonian of the system is given by

$$\hat{H} = V \sum_{n=0}^{L-1} (|n\rangle\langle n+1| + |n+1\rangle\langle n|) \quad (11.47)$$

with the real hopping parameter $V > 0$.

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with the real hopping parameter $V > 0$.

We consider periodic boundary conditions, i. e., we always identify

$$|n+L\rangle \equiv |n\rangle. \quad (11.48)$$

We want to find eigenvalues and eigenvectors of \hat{H} .

Proceed as follows:

- Due to the periodicity 11.48, indices can be always translated within a sum over lattice sites, i. e.

$$\sum_{n=0}^{L-1} f(n) = \sum_{n=0}^{L-1} f(n+m) \quad (11.49)$$

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- Show that the Hamiltonian is hermitian
- Consider the translation operator $\hat{T}(m)$ with the property (remember 11.48)

$$\hat{T}(m)|n\rangle = |n+m\rangle \quad (11.50)$$

Show that

$$\hat{H} = V(\hat{T}(1) + \hat{T}(-1)) \quad (11.51)$$

- consider the states

$$|\xi(k)\rangle = \sum_{n=0}^{L-1} e^{ikn} |n\rangle \quad (11.52)$$

Determine the allowed values of k for which 11.48 holds, and that gives different states $|\xi(k)\rangle$.

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- If the particle is prepared in the ground state, find the probability to find it in $|0\rangle$.

Solution:

Hermiticity:

$$\hat{H}^\dagger = V^* \sum_{n=0}^{L-1} (|n+1\rangle\langle n| + |n\rangle\langle n+1|) = \hat{H}$$

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as it is easy to show by applying it to an arbitrary $|n'\rangle$.Using 11.49, we can shift one of the terms of \hat{H} by one, obtaining

$$\hat{H} = V \sum_{n=0}^{L-1} (|n-1\rangle\langle n| + |n+1\rangle\langle n|) = V(\hat{T}(-1) + \hat{T}(1))$$

In order for the $|\xi(k)\rangle$ to have the correct periodic boundary conditions we must have (see 11.52) $e^{ik(n+L)} = e^{ikn}$, i. e.

$$k = \frac{2\pi j}{L} \quad j = 0, 1, \dots, L - 1$$

j must be integer and can be taken between 0 and $L - 1$. For $j = L$ we have $k = 2\pi$, which is equivalent to $k = 0$. We have, thus, L eigenvectors, as many as the dimension of the space.

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Applying $\hat{T}(m)$ to $|\xi(k)\rangle$:

$$\hat{T}(m)|\xi(k)\rangle = \sum_{n=0}^{L-1} e^{ikn}|n+m\rangle = \sum_{n=0}^{L-1} e^{ik(n-m)}|n\rangle = e^{-ikm}|\xi(k)\rangle$$

which shows that $|\xi(k)\rangle$ is an eigenvector of $\hat{T}(m)$ with eigenvalue e^{-ikm} .

Using [11.51](#), we have

$$\hat{H}|\xi(k)\rangle = V(\hat{T}(1) + \hat{T}(-1))|\xi(k)\rangle = V(e^{-ik} + e^{ik})|\xi(k)\rangle \quad (11.54)$$

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The minimum of the energy is given by $k = \pi$, where $E(\pi) = -2V$.

The corresponding eigenstate is $|\xi(\pi)\rangle$.

Using 10.3 with 11.52, we obtain that the probability $P(0)$ to find the particle in 0 is given by:

$$P(0) = \frac{1}{\langle \xi(\pi) | \xi(\pi) \rangle}$$

with

$$\langle \xi(\pi) | \xi(\pi) \rangle = \sum_{n,m} e^{-i\pi n} e^{i\pi m} \underbrace{\langle n | m \rangle}_{\delta_{n,m}} = L$$

so that $P(0) = 1/L$.

Some details



Probability density

[back](#) In terms of the probability density $P(x)$, the probability of finding x between x_1 and x_2 is given by

$$W(x_1 \leq x \leq x_2) = \int_{x_1}^{x_2} P(x) dx .$$

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If $x_2 = x_1 + \Delta x$, with Δx infinitesimal

$$W(x_1 \leq x \leq x_1 + \Delta x) = P(x_1)\Delta x \quad (12.1)$$

which defines $P(x)$.

Probability density

Three dimensional space

The extension to three dimensions is straightforward: In terms of the probability density $P(\mathbf{r})$, the probability of finding \mathbf{r} in a volume V is given by

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if $V = V(\mathbf{r}, \Delta V)$ is an infinitesimal volume of size ΔV around \mathbf{r} :

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Fourier representation of the Dirac delta

[back](#)

We prove the relation

$$\frac{1}{2\pi} \int e^{-ikx} dk = \delta(x) \quad (12.2)$$

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Transition from discrete to continuum

[back](#)

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We make here the example of the real-space basis $\{|x\rangle\}$, but it is easily extended to any continuum basis. We start by discretizing the domain of the possible values of x by a discretisation Δ that we will eventually let go to zero, i. e. we write

$$x_n = n \Delta \quad n = 0, \pm 1, \pm 2, \dots, \pm \infty . \quad (12.3)$$

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$$x_n = n \Delta \quad n = 0, \pm 1, \pm 2, \dots, \pm \infty . \quad (12.3)$$

We define corresponding discrete vectors $|\bar{x}_n\rangle$, which are (ortho-)normalized as usual discrete vectors:

$$\langle \bar{x}_n | \bar{x}_m \rangle = \delta_{n,m} = \delta_{n-m}$$

We now define new vectors, which differ just by a constant

$$|x_n\rangle \equiv \frac{1}{\sqrt{\Delta}} |\bar{x}_n\rangle .$$

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For $\Delta \rightarrow 0$ these are „continuum“ normalized [9.15](#), since:

$$\langle x_n | x_m \rangle = \frac{1}{\Delta} \delta_{n-m} \stackrel{\Delta \rightarrow 0}{=} \delta(x_n - x_m) . \quad (12.4)$$

The last step being valid in the $\Delta \rightarrow 0$ limit (see [12.8](#))

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We now consider the identity operator (see [9.25](#))

$$I = \sum_n |\bar{x}_n\rangle \langle \bar{x}_n| = \sum_n \Delta |x_n\rangle \langle x_n| \stackrel{\Delta \rightarrow 0}{=} \int |x_n\rangle \langle x_n| dx_n \quad (12.5)$$

Again, the last step is valid in the continuum $\Delta \rightarrow 0$ limit (see [12.7](#) below).

By inserting [12.5](#) we can obtain, for example, the continuum expression for the scalar product

$$\langle g|f\rangle = \sum_n \langle g|\bar{x}_n\rangle \langle \bar{x}_n|f\rangle = \int \langle g|x\rangle \langle x|f\rangle dx ,$$

where we have dropped the n indices, since the x are now continuous.

[back](#) Probability vs. probability density

We consider the expansion of a normalized state

$$|\psi\rangle = \sum_n \langle \bar{x}_n | \psi \rangle |\bar{x}_n\rangle$$

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$$|\psi\rangle = \sum_n \langle \bar{x}_n | \psi \rangle | \bar{x}_n \rangle$$

From [10.3](#), we know that the probability of obtaining x_n from a measure of \hat{x} is given by (the state is normalized)

$$W(x_n) = |\langle \bar{x}_n | \psi \rangle|^2 = \Delta |\langle x_n | \psi \rangle|^2 \quad (12.6)$$

Looking at [12.1](#), we can identify, in the $\Delta \rightarrow 0$ limit, $P(x) = |\langle x_n | \psi \rangle|^2$ as the **probability density**.

Some proofs for the continuum limit

We now prove the continuum limits carried out in [12.4](#) and [12.5](#).

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We have a smooth function $f(x)$, and we discretize x as in [12.3](#). We have

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Using this, we can write

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which lets us identify

$$\frac{\delta_{n-m}}{\Delta} \stackrel{\Delta \rightarrow 0}{\equiv} \delta(x_n - x_m) \quad (12.8)$$