Week ⓪

PHY 303 Quantum Mechanics
Instructor: Sebastian Wüster, IISER Bhopal, 2023

These notes are provided for the students of the class above only. There is no guarantee for correctness, please contact me if you spot a mistake.

0 Administrative affairs

(i) Office hours: Wed 2-4 pm. You can also meet me at other times, best drop an email before
Phone: 1213
Email: sebastian@iiserb.ac.in
webpage: http://home.iiserb.ac.in/∼sebastian/teaching.html

(ii) Literature:

- D. J. Griffiths, *Introduction to Quantum Mechanics* [GR] **the** textbook
- R. Shankar, *Principles of Quantum Mechanics*, [SH]
- J. J. Sakurai, *Modern Quantum Mechanics* [SA]

The course will mainly follow GR and SH. Where stray topics are taken from elsewhere I will try to indicate this.

(iii) Lectures and tutorials

- I am arranging lecture notes into "week" segments, based on similar content. While most of those segments should indeed take a week for us to work through, this will not be true for all and they may take less or more often more time. Some material makes explicit reference to my notes on PHY106, which are available on my webpage. With those you should easily be able to link this to the PHY106 lecture that you attended.
- One of the weekly sessions will alternate between tutorial and TA-class in studio AIR. (A) In one week we shall have a tutorial. In these we will do little tasks to understand the material more deeply. You should be up to date with the lecture material *prior* to a tutorial session. (B) The following week we shall do a TA-class/assignment class in which you present the solutions of assignments to each other. We will require everyone to present at least once, otherwise your final assignment score will be halved. We also require everyone, when asked, to be able to present solutions that carry their name. Either of these sessions are also implicitly Q&A sessions where you should ask your mates, the TAs and myself any questions you may have, ideally having generated those *before* during material revision.

(iv) Assessment:

- **2 scheduled Quizzes: 5%** There will be two quizzes lasting 50 min, to encourage you to keep on top of the material, both will count.
- **Assignments: 20%** There will be about five to seven assignments handed out with a two week deadline each. I expect you to form teams of 4-6 students and stick in these teams for the semester. Hand in only one solution per team. The TA is instructed to give full marks for *any serious attempt* at a given question of the assignment, even if the result is wrong. This is to discourage copying and encourage doing it yourself. However you will loose marks for not addressing parts of the question text, or if a mistake significantly reduces the required effort. The TA is also asked to deduct marks for messy presentation and blatant copying from anywhere. The same teams will be used in tutorials, see below. Submit your final assignment solution via email to the TA. All has to be integrated in a single file, e.g. pdf. This may be a good opportunity to learn LaTex and nicely typeset your solution, but handwritten and good-quality scanned/photographed is fine too. By mutual agreement with TA, we can handle hardcopies too. *See also notes below about TA class.*
- **Numerics component of assignments:** Moderns science almost always necessitates the heavy use of computers. Most assignments will contain a numerics component, targeting mathematica for which I may prepare templates. Porting these to any other language of your preference is fine. Please make the campus license version downloadable from the CC webpage available on at least one computer accessible to your team. You shall also need VPN access to the campus network for the license. For each assignment, I will often provide a template code package that you have to only minorly edit. See notes on numerics assignments online.
- **TA class and tutorial attendance: 5%** Attending these events is compulsory. When attendance is less than 60% the marks for this component are 0, and for more than 90% they are 100. In between they are as per fractional attendance.
- **Mid-sem exam: 30%, Final exam: 40%** The exams will try to test understanding of the essential *physics* concepts taught, not maths. For guidance regarding what are the most important concepts look at the quizzes, assignments and tutorials. All exams will be designed to give a significant advantage to those students that solved all tutorials and assignments by *themselves* within their team.

The final allocation of grades will be *relative*, which means that I look at the distribution of total marks, and accordingly allocate the cut-offs for the grades.

0.1 Course Outline

PART 1 (PHY303)

1) **Motivation, foundations and review:** $\sim$ 3 weeks
• Why do we need to know more about quantum mechanics than we learnt in PHY106? Review of basic probability theory, linear algebra and function vector spaces. Schrödinger's equations, position versus momentum space. Expectation values.

2) **Solvable quantum problems in one dimension:** ∼ 3 weeks
   - The square well potential, harmonic oscillator, tunneling, free particle

3) **Mathematical Interlude:** ∼ 2 weeks
   - Commutators, simultaneous diagonalisation, generalised uncertainty principle, pictures for time-evolution

4) **Quantum mechanics in three dimensions:** ∼ 4 weeks
   - Angular momentum, Hydrogenic atoms, spin, angular momentum additions

5) **Multi-particle systems:** ∼ 2 weeks
   - indistinguishable particles, non-classical correlations

PART 2 (PHY304)

6) **Mathematical Interlude II:** ∼ 2 weeks
   - Motivation, Symmetries and conservation laws

7) **Approximation methods for time-independent problems:** ∼ 4 weeks
   - Time independent perturbation theory, variational method, WKB approximation

8) **Quantum scattering theory:** ∼ 2 weeks
   - Born approximation, partial wave decomposition

9) **Quantum dynamics:** ∼ 3 weeks
   - Time dependent perturbation theory, Fermi's golden rule, adiabatic theorem

10) **Advanced topics:** ∼ 2 weeks
   - Basic Gauge theory, Charged particle in an electromagnetic field, Relativistic quantum mechanics

Contents

0.2 Math content

Moving from year 2 to year 3 at IISERB and into your physics major, you will experience a signifiant upwards jump of the level of mathematics in most courses, certainly in this one. I will expect you to be familiar with the following math topics:

- vectors, scalar-products, norm of vectors
- matrices, eigenvalues and eigenvectors of matrices
- Solutions of basic ordinary differential equations
- complex numbers
- basic differentiation and integration

Where you have doubts about being sufficiently familiar with any of those, please consult your math course notes, books or online resources. Focus on books/courses of the kind “mathematics for scientists and engineers” that tell you “how to actually get calculations done”. An exemplary online resource is e.g. this link

For the following required math tools, I shall attempt to give a small self contained introduction:

- probability theory
- non-cartesian / curvilinear coordinate systems
- function vector spaces, advanced linear algebra
- solutions of partial differential equations
- boundary value problems, solutions through power series
- Dirac delta function

1 Motivation, foundations and review

1.1 Motivation

- You have learnt in PHY106 that the concepts of classical physics are unable to explain the details of a couple of key experiments/phenomena, such as the photo-effect, black-body radiation and the stability of the atom. We will not repeat discussions of these historical developments and experiments here, please revisit PHY106 week 4,5 for all items you might have forgotten.
- To make room for that presentation of historical developments, and to reflect the fact that PHY106 is taken by all IISERB students (also non PHY/MTH majors), we had reduced the emphasis on the mathematical formalism there to a large extent.
- This course will introduce the math behind quantum mechanics in much greater depth, and then revisit all the key scenarios you already briefly encountered in PHY106 in detail. Essentially, whereever earlier we had just shown you results without proof, now we will show you the "why".
- Very important examples for which we will supply derivations missing earlier are Eq. 107(c) (PHY106, week 8), the quantum harmonic oscillator (PHY106, week 9) and the Hydrogen wave functions (PHY106, week 10) [1].
- Another major aspect that deserves much more attention, is the handling and interpretation of measurements in quantum mechanics.
- I also encourage you to (re-)watch the list of motivational videos below. Some aspects discussed there were touched by PHY106, but some more will be now: Powers of ten
  The secrets of quantum physics
  Quantum theory made easy (part I)
  Quantum theory made easy (part II)
  Many explanations in these movies are too fast and others too basic. However they communicate that quantum mechanics is exciting and mind-boggling.

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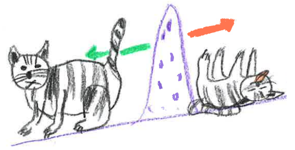
[1] I shall refer to the material of PHY106 frequently, please refer to my webpage (2019-20-II Semester)

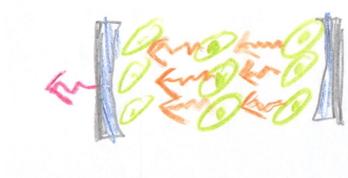
Decoherence and quantum classical transition

- Schrödinger's cat
- Why the world around us appears classical



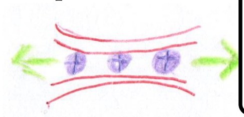
Spectroscopy and probing

- NMR, Tunneling microscope
- Lasers



Quantum information

- Entanglement
- Quantum computation



- Quantum cryptography

Quantum statistical physics

- Bose-Einstein condensates
- degenerate Fermi gases

PHY303 Quantum mechanics

- Bound states, discrete energies
- Quantum superpositions
- Wavepackets
- Angular momentum addition
- Entanglement
- Quantum mechanical measurement

The bubble diagram here gives an idea of the central role played by "quantum mechanics" throughout most of modern physics.

Atomic, molecular and optical physics

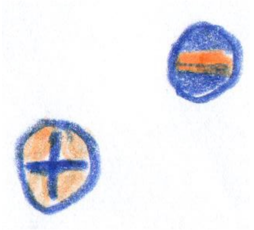
- Periodic table
- Molecular bonds
- Quantum optics

Solid state and material science

- quantum materials
- band structure, phonons,
- quasiparticles, excitons, magnons, plasmons
- magnetism, superconductivity

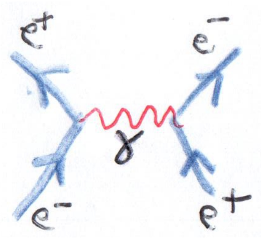
Relativistic quantum mechanics

- Dirac equation
- Spin
- Anti-particles



Quantum Field theory

- Gauge principle
- Particle creation and conversion



Nuclear and particle physics

- Super heavy elements, Nuclear fusion
- Neutron stars
- Exotic particles

1.2 Research frontier

- Pretty much all the advanced topics mentioned in the previous diagram are at the current research frontier with lots of activity.
- However even among the central box, i.e. the formalism of quantum mechanics and hence the present course, there are open questions, such as
  - How can we better describe a measurement in the quantum mechanical formalism?
  - How can we overcome the exponential scaling of a many-body Hilbertspace in computational approaches?
  - Is there some criterion that delineates macroscopic bodies behaving classically and microscopic ones quantum mechanically, or do really all bodies behave quantum mechanically? See e.g. this video .

1.3 Fundamental extensions of quantum mechanics (not in this course)

Already some flashed in previous boxes...

- In this lecture we will restrict ourselves to non-relativistic quantum mechanics, with velocities $v \ll c$, or energies $E \ll mc^2$. However quantum mechanics can be formulated adhering to the laws of special relativity and is then called "relativistic quantum mechanics", we will peep into this topic at the end of PHY304, or it would be more thoroughly covered in particle physics or quantum field theory lectures.
- We will also focus on single particle or few particle physics. Quantum mechanics usually requires advanced solution methods to deal with truly many particles, as for example required in condensed matter physics or quantum chemistry.
- Both concepts (relativity and many particles or uncertain particle numbers) are then combined in lectures on "quantum field theory".
- You recover classical mechanics from quantum mechanics in the limit $S/\hbar \to \infty$, as I shall mention occasionally. Also see week 11 of the PHY305 "classical mechanics" lecture notes on my webpage (only at the end of this semester, if you are interested).

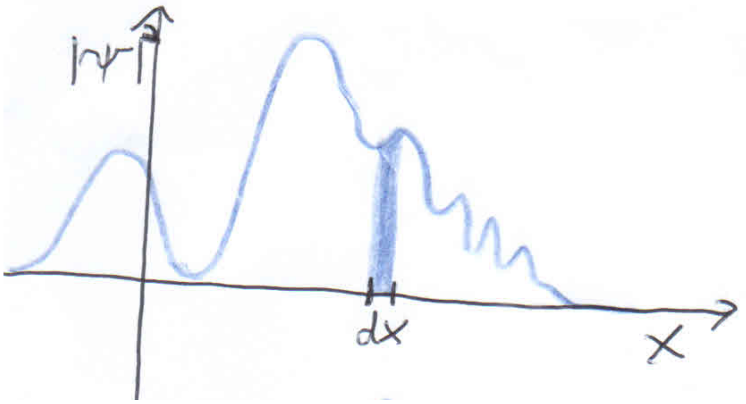
1.4 From classical to quantum mechanics

This section is a brief reminder or summary of PHY106, and intended as motivation for the math background in section 1.5.

The state of a particle: In classical mechanics we know everything about a particle if we specify its position $\mathbf{x}(t)$ and velocity $\mathbf{v}(t)$ (or momentum $\mathbf{p}(t)$). In PHY106 you learnt about a few key experiments (the photo effect, black body radiation, Compton scattering etc.) that forced us to develop quite different ideas. Instead of the above, all particles are in fact at the same time also waves. These are called matter waves. Mathematically we replace a well defined position and velocity by the

Wavefunction (or quantum state) of the particle. We shall write $\Psi(x,t)$ for a generic wavefunction that depends on one spatial coordinate x and time t.

- $\Psi(x,t)$ is a probability wave. That means that we consider $|\Psi(x,t)|^2 dx$ as the probability to find the particle in a small interval dx near the position x, see figure below. We say that $\rho(x,t) = |\Psi(x,t)|^2$ is the probability density for a measurement of the position of the particle (see section 1.5.2) at time t.



left: Exemplary probability density of particle position, for a particle with wavefunction $\Psi(x,t)$.

- Please review PHY106 weeks 5,6 for the reasons why we arrived at this picture. In short: To explain all experiments one has to attribute wave properties also to particles. The probability interpretation is then one that simply works, however there are a few aspects with which people have misgivings.

- Note that the wavefunction itself is a complex function, so by itself it cannot be related to a probability.

Dynamics of a particle: To find how the classical state $(\mathbf{x}(t), \mathbf{p}(t))$ changes in time, we can use Newton's equation

$$m\ddot{\mathbf{x}}(t) = \mathbf{F} = -\boldsymbol{\nabla} V(\mathbf{x}), \tag{1.1}$$

where m is the particle mass, $\mathbf{F}$ is the force, given by the gradient $\boldsymbol{\nabla}$ of the potential $V(\mathbf{x})$. The corresponding equation of motion for the wave function in quantum mechanics is

Schrödinger's equation (time dependent Schrödinger equation, TDSE), given by

$$i\hbar \frac{\partial}{\partial t}\Psi(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\Psi(x,t). \tag{1.2}$$

- The TDSE is of first order in time derivatives. This means we can solve it as an initial value problem: If we know the initial wavefunction $\Psi(x,t=0)$, the equation uniquely determines the wavefunction $\Psi(x,t)$ at all later times.

- The left hand side contains the imaginary unit i, we thus require complex numbers to solve it. It also contains the reduced Planck's constant $\hbar = h/(2\pi) = 1.0546 \times \times 10^{-34}$ Js, where Planck's constant h is

$$h = 6.626 \times 10^{-34} \text{ Js}. \tag{1.3}$$

  It has units of "Energy × times", which you shall learn in PHY305 is called an action. We shall see that for actions S of a problem with $S \sim \hbar$, quantum effects such as discrete energy states are usually crucial, while for $S \gg \hbar$ one recovers classical mechanics.

- In the same way that one cannot derive Newton's equation from any deeper principles, that is also not possible for Schrödinger's equation (1.2) [2] . However we went through some argumentation in PHY106 why the equation is reasonable to describe matter waves.

- We will see later, than one usually starts quantum mechanics by assuming its validity (and a few other so-called postulates). So far, the equation has passed every single experimental test.

- While the description of physics appears entirely distinct from Newtonian mechanics, the TDSE entails all the same essential physics (see example below), plus some new features, due to interference (which is only possible for waves).

Even in one dimension, analytical solutions of (1.2) can be found only for a few special cases, we will cover almost all of these in this lecture. However it is straightforward to solve it on a computer. Please revisit the following example in week 8 of PHY106

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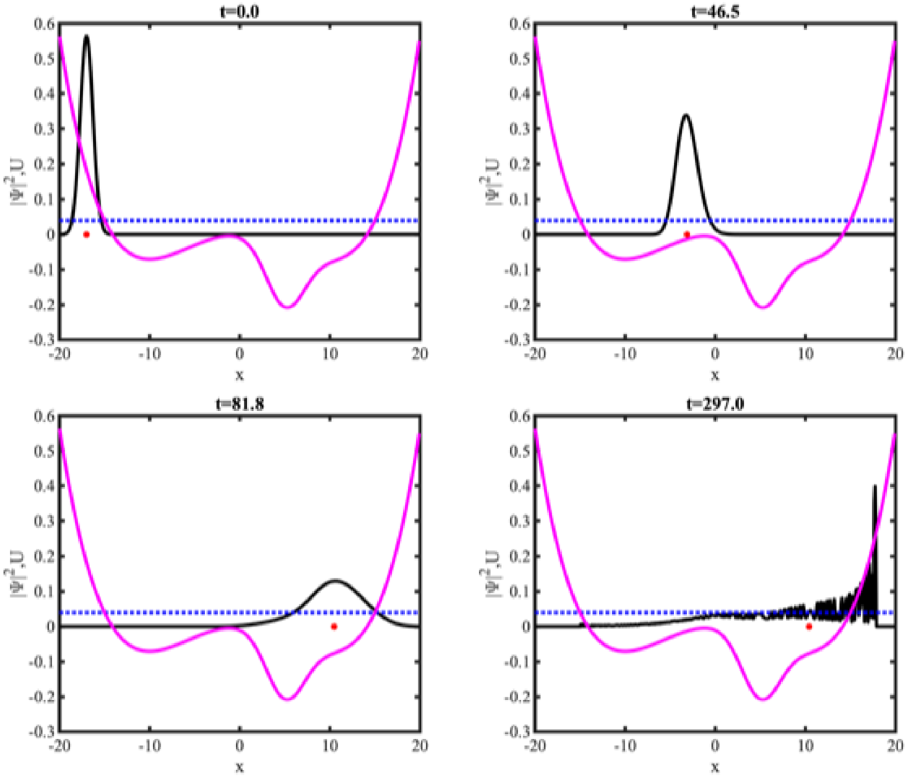
[2] Except perhaps the principle of minimal action, which yields both equations and more, and about which you will learn in PHY304 *classical mechanics*. However this just shifts the part that we cannot further derive from one equation to the next.

Example 1, Numerical solution of Schrödinger's equation: In the frames at different times below, we show $V(x)$ (magenta) $|\Psi(x,t)|^2$ (black), E (blue dashed) and $x(t)$ from Newton's equation (red dot).



This course will teach you how to solve this, but for now the message is that the "mean location" of the particle actually follows the same rules as it would classically. However, in addition to that, quantum mechanics always describes an uncertainty (standard deviation) of this location, which can also change in time. Finally, it adds interference effects, which do not exist classically, see the last frame.
Please see the full movie on the webpage.

Interpretations of quantum mechanics:

According to the above, the wavefunction $\Psi(x,t)$ only gives us probabilistic information about the particle, in contrast to the certainties that we are used to from classical mechanics. This has been irritating scientists for long, and still does, leading to several different so-called "interpretations of quantum mechanics"[3] Suppose we had a particle in wavefunction $\Psi(x,t)$ and measured it to be at location x_0. We now want to ask "where was the particle before the measurement". Following Griffith, the main interpretations then differ as follows

(i) Realist: It already was at x_0, but we somehow could not know. In this interpretation, we assume quantum mechanics is just not all of the truth, and probabilities $\rho(x)$ arise due to incomplete information (or so called "hidden variables").

(ii) Orthodox (Copenhagen interpretation): The particle was nowhere specific. Only through the

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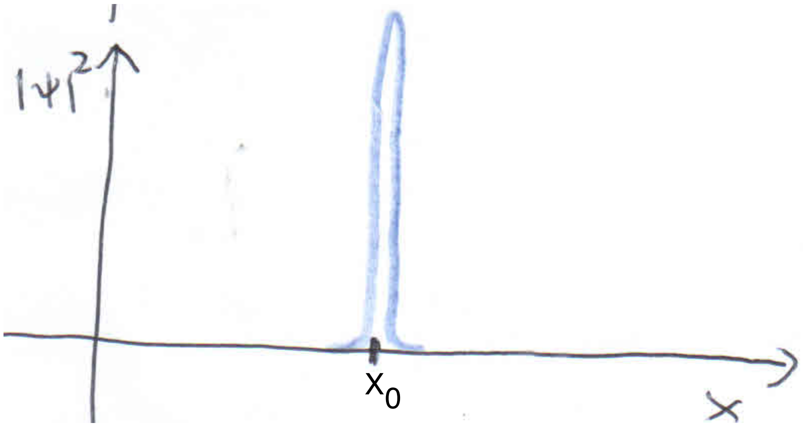
[3] As opposed to "math of quantum mechanics". Of that, there is only one, and it works.

act of measurement do we force it to take a specific position. This position later remains re-producable (if we measure the position again) (*). This interpretation attributes a very special role to the act of measurement, why a "measurement" would be so special is still unresolved.

(iii) Agnostic: One does not want to worry about it, since it is logically impossible to measure what the position of the particle before the measurement was.

We shall follow (ii) here, as is usually done, since local realism (hidden variable theories) have been ruled out by many experiments based on Bell's theorem, which we shall briefly visit in chapter 5.

In order to ensure (*) above, that measurements once done are reproducable afterwards, one has to assume the collapse of the wavefunction. If a particle had a wavefunction as in the figure on page 9, we then measure its position to be x_0, the act of measurement changes the wavefunction to one very sharply peaked around x_0 as shown below.



left: Suppose a particle had the wavefunction on page 9, and then we measured it to be at position x_0. The act of measurement has collapsed the wavefunction to the one shown, peaked around x_0 up to the measurement resolution.

Again, this behaviour cannot be derived but has to be postulated, and describes all available experiments. The fact that measurements perturb the quantum states of the object being measured, is central to quantum mechanics.

Week ①

PHY 303 Quantum Mechanics
Instructor: Sebastian Wüster, IISER Bhopal, 2023

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1.5 Mathematical Foundations of Quantum mechanics

In the previous week, we got reminded that quantum physics involves probability theory and wavefunctions in a central way. Let us thus briefly review (or provide) the essential math to deal with both of these. For this we have preponed some of Griffith chapter 3, particularly 3.2. You can find many other QM books that do all the math at the beginning, we will still leave most of it for our chapter 3 later, as Griffith does.

1.5.1 Complex numbers

I shall assume you know complex numbers from math courses. The following are the absolute bare essentials provided for sake of completeness and to define notation. If we later use anything related to complex numbers that you had not seen before, please let me know. I might then include those points in this section. See also PHy106, week 8.

Quantum mechanics involves complex numbers in an essential way. A complex number can be written as $z = x + iy$, where the imaginary unit i is defined via $i = \sqrt{-1}$. We then call $x = \mathfrak{Re}[z]$ the real part and $y = \mathfrak{Im}[z]$ the imaginary part of z. Since it has two components, we can draw each complex number as a 2D vector (x, y) in a 2D space called the complex plane. That also makes apparent that we can write it in polar notation $z = re^{i\varphi}$, where $0 \leq r$ is a real amplitude and $0 \leq \varphi \leq 2\pi$ a real phase.

Each complex number has what is called its complex conjugate denoted by z^* which is $z^* = x - iy$ (i.e. we just flip the sign of the imaginary part). With this we can find the modulus of a complex number as $|z| = \sqrt{z^* z} = \sqrt{x^2 + y^2}$, just as would be the case for a 2D vector.

A very useful equation is Euler's equation:

$$e^{iz} = e^{-y+ix} = e^{-y}[\cos(x) + i\sin(x)]. \tag{1.4}$$

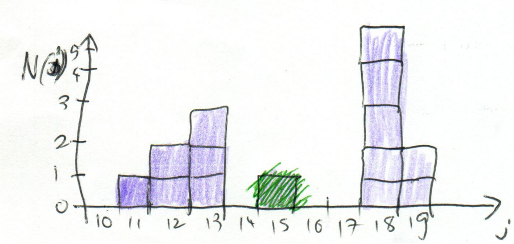
1.5.2 Probability theory

Here we only establish the most important concepts of probability theory, to have everyone on the same page.

Probabilities Consider a random variable j with discrete/integer outcomes. Suppose we draw from a set of N elements, where outcome j is contained $N(j)$ times. Clearly $N = \sum_j N(j)$. The probability of outcome j is then $P(j) = N(j)/N$. All the values $P(j)$ together are called a probability distribution. The average (mean) outcome is

$$\langle j \rangle = \sum_j P(j) j. \tag{1.5}$$

Example 2, Age of computer players: (discrete) Consider the following set of players of some online computer game, with ages: 11, 12 (×2), 13 (×3),15, 18 (×5), 19 (×2). For this set, we can draw the histogram below.



left: Histogram of the number of occurrences $N(j)$ of event j (here j =age), within a sample of 13 players. [Ignore the green box at 15]

Using $P(j) = N(j)/N$ we find e.g. the probability that a randomly chosen player has age 13 to be $P(13) = 3/13$ =23%. The mean age turns out to be 14.4, it gives an indication of the centre of the probability distribution. The mean is not to be confused with the most likely outcome, which is here 18. In fact, there is no outcome possible near the mean value (for 14,15) at all! Another concept would be the median which is the value j for which the probability of a higher result equals that of a lower result[a]

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[a] This is not used as much in quantum mechanics.

Above we dealt with random variables that take integer values. For continous outcomes x we define

Probability densities Consider a random variable x with continuous outcomes. We describe those with a probability density $\rho(x)$ such that the probability for the outcome to lie between x and $x + dx$ is given by $\rho(x)dx$. The probability for the result to lie between a and b then is $P_{ab} = \int_a^b \rho(x)dx$.

The

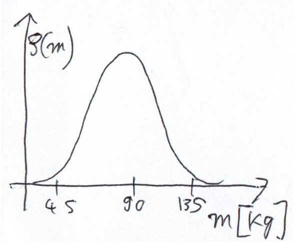
Mean of the probability density is

$$\langle x \rangle = \int_{-\infty}^{\infty} x\rho(x)dx \tag{1.6}$$

- In quantum mechanics, we usually refer to the mean as expectation value.
- Clearly the probability to have an arbitrary (unspecified) outcome has to be 1. This implies $\sum_j P(j) = 1$ (discrete) or $\int_{-\infty}^{\infty} \rho(x)dx = 1$ (continuous).

- From the definition $P(j) = N(j)/N$ it is obvious that a probability has to be a positive real number (since the same is true for the "number of some items"). Saying the probability for an event is -5% makes as little sense as saying "I own -5 cars". We state probabilities are positive and real here so clearly, since it provides a very imporant sanity check for many quantum mechanical calculations, that DO involve negative and complex numbers. Hence the slightest mistake might make a probability that you try to calculate negative, but you always *know* then, that a mistake has happened.

Example 3, Weight of computer players: (continuous) Weight can take any value, not just integers.



left: An exemplary continuous probability distribution for the weight of an average human is shown on the left (possibly unrealistic).

Using e.g. the formula $P_{ab} = \int_a^b \rho(x)dx$, we can infer information such as "the probability for the weight to be > 88 kg is 50%.

- Comparing example 2 and example 3: Physically, of course the age was also a continuous quantity. We had referred to the custom of giving an integer age for a person, rounding down.
- Be aware, that the figures are showing two quantities of slightly different character, example 2 shows a histogram for the number of occurrences within a finite sample size of $N = 13$, while example 3 discusses a probability distribution that does not refer to a specific sample size.

An important property of a histogram, probability distribution or probability density is how "scattered it is". For example the set of outcomes [3,50,123,555] varies very widely (large scatter), while outcomes [122,123,123,124] are much less scattered. To quantify this we use the following

Measures for the width of a probability distribution

The variance σ^2 of a probability distribution is

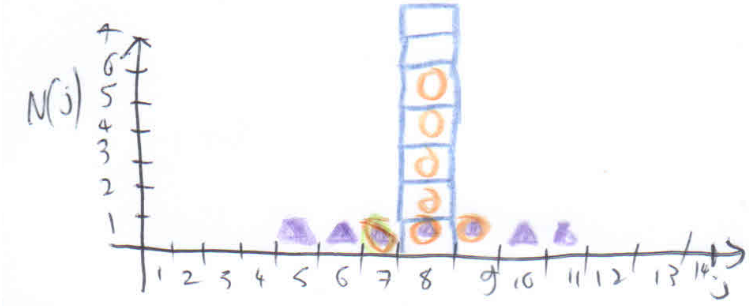
$$\sigma^2 = \text{Var}[P] = \langle (j - \langle j \rangle)^2 \rangle = \sum_j P(j)(j - \langle j \rangle)^2, \qquad \sigma^2 = \int dx\, \rho(x)(x - \langle x \rangle)^2 \tag{1.7}$$

in the discrete and continuous cases respectively. From these, we define the standard deviation

$$\sigma = \sqrt{\text{Var}} = \sqrt{\langle (j - \langle j \rangle)^2 \rangle}, \qquad \sigma = \sqrt{\int dx\, \rho(x)(x - \langle x \rangle)^2} \tag{1.8}$$

- The variance adds up the squares of the deviation $j - \langle j \rangle$ from the mean.
- Exercise: One can show that $\sigma^2 = \langle j^2 \rangle - \langle j \rangle^2$ (for both discrete and continuous). This formula is usually easier to use than the direct definition.
- The standard deviation gives a measure of the width of a probability density. Not to be confused with the standard error $\sigma/\sqrt{N}$, which gives the error of the mean $\langle j \rangle$.

Example 4, Varying width of probability distribution: Below are three age distributions such as in example 2,

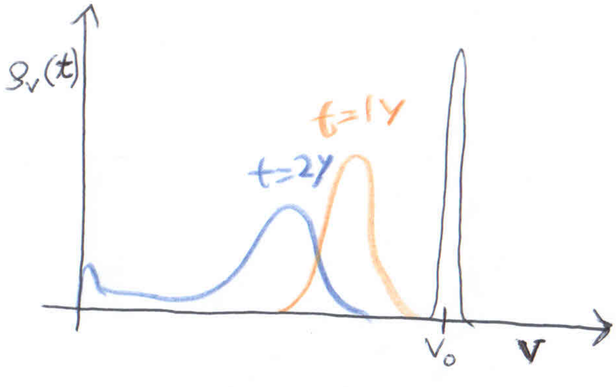


left: drawn with symbols (i) blue squares (ii) red circles (iii) violet triangles.

If you would calculate the mean according to Eq. (1.5), you'd find the same answer ($\langle j \rangle = 8$) for each. However the standard deviations using (1.8) are (i) $\sigma = 0$ (ii) $\sigma = 1/\sqrt{3}$ (iii) $\sigma = \sqrt{14/3} \approx 2$. You can see how the standard deviation gets larger for wider distributions. It roughly correspond to the (half) width of the distribution.

Time dependence of probability distributions: Nature offers many examples of probability distributions that (may) depend on time, we will see many of those in quantum mechanics. An example in a totally different context is given below:

Example 5, Value degradation of a car: Cars quickly loose value on the second hand market after purchasing them. The figure below shows the value distribution of a certain model at three different times.



left: Value v of a car model at the moment of purchase (black), after one year (brown) and after two years (blue).

initially there is only a small spread due to different vendor margins. After one years, cars loose value since they age, but also the width of the distribution increases as cars experiences different mishaps such as scratches.

1.5.3 Vector spaces and matrices

For handling wavefunctions in quantum mechanics, it is very useful to realize that these wavefunctions can be viewed as vectors, which we shall explain in section 1.5.4. You will be familiar with the concept of a vector space from linear algebra, most often dealing with 3-component (3D) vectors $\mathbf{v} = [v_x, v_y, v_z]^T$ that can label a point in 3D space, let us first briefly review those concepts in the present section.

Vector space: A vector space V over a field[a] F is a set of objects with an addition operation "+" (of two vectors $\mathbf{v} \in V$) and a multiplication operation "×" (of an element in the field $f \in F$ and a vector). The operations have to fulfill the following axioms (for $\mathbf{u}, \mathbf{v}, \mathbf{w} \in V$ and $a, b \in F$)

(i) $\mathbf{u} + (\mathbf{v} + \mathbf{w}) = (\mathbf{u} + \mathbf{v}) + \mathbf{w}$ (associativity of +)

(ii) $\mathbf{u} + \mathbf{v} = \mathbf{v} + \mathbf{u}$ (commutativity of +)

(iii) $\exists \mathbf{0}$ such that $\mathbf{v} + \mathbf{0} = \mathbf{v}\ \forall \mathbf{v}$ (identity element of +)

(iv) $\exists {-\mathbf{v}}$ such that $\mathbf{v} + (-\mathbf{v}) = \mathbf{0}\ \forall \mathbf{v}$ (inverse element for +)

(v) $a(\mathbf{u} + \mathbf{v}) = a\mathbf{u} + a\mathbf{v}$, and $(a + b)\mathbf{u} = a\mathbf{u} + b\mathbf{u}$ (distributivity of scalar multiplication)

(vi) $1\mathbf{v} = \mathbf{v}$ (where 1 denotes the multiplicative identity in the field)

(vii) $a(b\mathbf{v}) = (ab)\mathbf{v}$ (compatibility of scalar multiplication with field multiplication)

We have used the usual notation not to write the × symbol explicitly.

[a] e.g. type of numbers, such as real or complex numbers

- The example you probably know best is $\mathbb{R}^3$, the set of three-component real column vectors $\mathbf{v} = [v_x, v_y, v_z]^T$, that can define a point in 3D space[4]. Here we use the operation "+" as $\mathbf{v} + \mathbf{u} \equiv [v_x + u_x, v_y + u_y, v_z + u_z]^T$ and $a \times \mathbf{v} \equiv [au_x, au_y, au_z]^T$. You can verify that these objects and operations fulfill all the axioms in the definition above.

- Note that the complex numbers also form a field, so the first generalisation we will do in the following is to allow a, b and the column entries of the vectors to be complex.

- An important concept in a vector space is that of orthogonality, which we define via the scalar product

  $$\mathbf{v}^* \cdot \mathbf{u} = v_x^* u_x + v_y^* u_y + v_z^* u_z, \tag{1.9}$$

  calling vectors orthogonal when $\mathbf{v}^* \cdot \mathbf{u} = 0$.

- Another important concept is the norm of a vector, which we define as $||\mathbf{v}|| = |\mathbf{v}| = \sqrt{|\mathbf{v}^* \cdot \mathbf{v}|}$.

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[4] Here ^{T} indicates the "transpose". I.e. $[v_x, v_y, v_z]^T = \begin{bmatrix} v_x \\ v_y \\ v_z \end{bmatrix}$

- The last two dotpoints can also be defined via a set of axioms (which we defer to section 3.2). The advantage of all these axioms, is that they then allow the generalisation of these concepts to any objects fulfilling them. We want to use this very shortly, to apply them all to wavefunctions.

Every vector space V has a

Basis: as a set $\mathcal{B}$ of d linearly independent vectors $\mathcal{B} = \{\mathbf{b}_n\}$ that spans the space, which means we can write every $\mathbf{v} \in V$ as

$$\mathbf{v} = \sum_{n=0}^{d-1} v_n \mathbf{b}_n, \tag{1.10}$$

for some suitable coefficients $v_n \in F$.

- Each vector space can have many different bases.
- We call the number of elements d in the basis $\{\mathbf{b}_n\}$ the dimension of the vector space.
- Special bases are orthonormal bases, that fulfill $||\mathbf{b}_n|| = 1$ and $\mathbf{b}_n^* \cdot \mathbf{b}_m = \delta_{nm}$. We can then find the coefficients for Eq. (1.10) using $v_m = \mathbf{b}_m^* \cdot \mathbf{v}$ (exercise).
- Again going to the example $\mathbb{R}^3$, you would usually think of the orthonormal basis $\{\mathbf{i}, \mathbf{j}, \mathbf{k}\}$ for $\mathbf{i} = [1,0,0]^T$, $\mathbf{j} = [0,1,0]^T$, $\mathbf{k} = [0,0,1]^T$, but could equally well choose $\{\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3\}$ with $\mathbf{b}_1 = \frac{1}{\sqrt{3}}[1,1,1]^T$, $\mathbf{b}_2 = \frac{1}{\sqrt{6}}[1,-2,1]^T$, $\mathbf{b}_3 = \frac{1}{\sqrt{2}}[1,0,-1]^T$, which is also orthonormal (exercise).

When working with vectors, one often also ends up dealing with matrices. You may know an $n \times m$ matrix firstly as a rectangular array (tableaux, grid) of numbers with n rows and m columns. However mathematicians would rather define a matrix via a:

Linear transformation: A linear transformation T is a map from an N dimensional vector space V to an M dimensional one W:

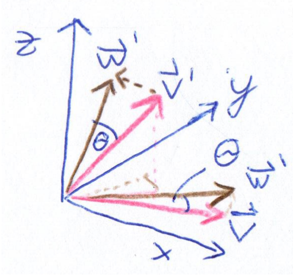
$$T : \mathbf{v} \to T(\mathbf{v}) = \mathbf{w}, \tag{1.11}$$

that maps vectors $\mathbf{v} \in V$ onto those $\mathbf{w} \in W$, and is linear, which means:

$$T(a\mathbf{v} + b\mathbf{w}) = aT(\mathbf{v}) + bT(\mathbf{w}). \tag{1.12}$$

For any deeper discussion of linear transformations we refer to linear algebra books or courses.

Example 6, Rotations: One example of a linear map are rotations in $\mathbb{R}^3$:



left: A rotation by an angle θ around the z-axis uniquely allocates a rotated vector $\mathbf{w}$ (brown) to each input vector $\mathbf{v}$ (pink).

We mostly require the case in the following, where both vector spaces are identical $V = W$, so we shall assume that in the following. It turns out that we know everything about a linear transformation, if we know what it does with each orthonormal basis vector. To see this, let us apply it to one of them:

$$T(\mathbf{b}_j) = \sum_{i=1}^{d=N} T_{ij}\mathbf{b}_i. \tag{1.13}$$

Here we have used the fact that, regardless of what the map does, we can write the result again in the basis $\mathcal{B}$. Using the orthonormality of the basis, we can find the coefficients $T_{ij} = \mathbf{b}_i^* \cdot T(\mathbf{b}_j)$, i.e. by "projecting" Eq. (1.13) onto the basis vector $\mathbf{b}_i$. Let us now write both, an arbitrary input vector $\mathbf{v}$ and output vector $\mathbf{w}$ of the transformation in the basis $\mathcal{B}$, i.e. $\mathbf{v} = \sum_k v_k\mathbf{b}_k$ and $\mathbf{w} = \sum_i w_i\mathbf{b}_i$. We then see that:

$$T(\mathbf{v}) = T(\sum_k v_k\mathbf{b}_k) \overset{Eq.\ (1.12)}{=} \sum_k v_k T(\mathbf{b}_k) \overset{Eq.\ (1.13)}{=} \sum_k v_k \sum_i T_{ik}\mathbf{b}_i \equiv \sum_i \underbrace{w_i}_{=\sum_k T_{ik}v_k} \mathbf{b}_i. \tag{1.14}$$

We thus know all the coefficients $w_i = \sum_k T_{ik}v_k$ in the basis expansion for $\mathbf{w}$ in terms of those of $\mathbf{v}$ and the numbers T_{ik}.

We can write these as a

Matrix: A matrix $\underline{\underline{M}}$ is an $N \times M$ table of numbers M_{ik}, where i numbers the row and k the column. The numbers ik are called matrix elements.

- As per discussion before, we can view every matrix as a representation of a linear transformation using specific bases.
- You recognise $w_i = \sum_k T_{ik}v_k$ as the component notation for the vector matrix product $\mathbf{w} = \underline{\underline{T}} \cdot \mathbf{v}$.
- Griffith reminds you of all these things only in section 3.1.3. I would encourage you to jump ahead there if you wish to. Do not be disturbed by the notation used, where they write $|\,v\,\rangle$ instead of vector $\mathbf{v}$ (just swap the notation in your head). We shall discuss the reason for that notation in section 3.1 later.

Example 7, Rotation matrices: We can again look at example 6 and thus now infer, that for the linear transformation "rotation around z-axis by angle θ", there exists a specific matrix (called rotation matrix) $\underline{\underline{O}}_z(\theta)$, which provides $\mathbf{w} = \underline{\underline{O}}_z(\theta)\mathbf{v}$ and $\mathbf{w}' = \underline{\underline{O}}_z(\theta)\mathbf{v}'$. Note that this is a single matrix, that rotates all vectors correctly. *If you have a deeper interest, see my notes for PHY305, section 3.4 .*

Throughout physics, we make extensive use of the

Matrix eigenvalue equation:

$$\underline{\underline{M}} \cdot \mathbf{v}_k = \lambda_k \mathbf{v}_k, \tag{1.15}$$

for a square matrix $\underline{\underline{M}}$, with eigenvectors $\mathbf{v}_k$ for eigenvalues λ_k.

- The subscript k indicates that an $n \times n$ matrix can have multiple eigenvectors and eigenvalues, up to n.
- Sometimes, multiple eigenvectors share the same eigenvalue. That eigenvalue is then called degenerate.
- We skip a review here on how to practically find the eigenvalues and eigenvectors of a given matrix. However it will be important for this course. If you are not 100% comfortable, please consult your favorite linear algebra book or course, or Griffith section 3.1.4. For assignments it will typically be permitted and recommended to find eigenvalues and eigenvectors with a computer, for this get your copy of `mathematica` from the CC webpage and learn about the command `EigenSystem`.

We will deal here mostly with complex square matrices. Even for that subset, there are lots of different types of matrices that have their own name, which you are reminded of in the following[5]:

Special matrices:

Symmetric matrices: $\underline{\underline{S}} = \underline{\underline{S}}^T$, Hermitian matrices: $\underline{\underline{O}} = \underline{\underline{O}}^\dagger$,

Orthogonal matrices: $\underline{\underline{O}} \cdot \underline{\underline{O}}^T = \mathbb{1}$, Unitary matrices: $\underline{\underline{U}} \cdot \underline{\underline{U}}^\dagger = \mathbb{1}$.

Finally we are in a position to make the statement for which we have included section 1.5.3. If you don't like any of the above, just remember the following

Eigenvectors of a Hermitian matrix: A $N \times N$ Hermitian matrix $\underline{\underline{O}}$ with $O_{ij} \in \mathbb{C}$ has exactly N eigenvectors with real eigenvalues (not necessarily different). These eigenvectors $\{\mathbf{v}_k\}$ form a basis of the vector space $\mathbb{C}^N$.

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[5] Here ^{T} indicates the "transpose". I.e. $\begin{bmatrix} a & b \\ c & d \end{bmatrix}^T = \begin{bmatrix} a & c \\ b & d \end{bmatrix}$ and † the "complex adjoint" (transpose with complex conjugation) $\begin{bmatrix} a & b \\ c & d \end{bmatrix}^\dagger = \begin{bmatrix} a^* & c^* \\ b^* & d^* \end{bmatrix}$

Finally, for many[6] matrices one can do a

Matrix diagonalisation: We write the matrix $\underline{\underline{M}}$ as a product

$$\underline{\underline{M}} = \underline{\underline{O}} \cdot \underline{\underline{D}} \cdot \underline{\underline{O}}^{-1} \tag{1.16}$$

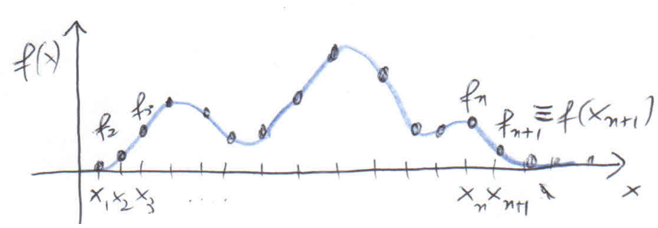
where $\underline{\underline{D}}$ is a diagonal matrix which contains the eigenvalues λ_k on the diagonal (see Eq. (1.15)), and $\underline{\underline{O}}$ is an orthogonal matrix (see box above), which contains the unit normalized eigenvectors as columns, i.e. $\underline{\underline{O}} = [\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3]$.

- Importantly for us, later, Hermitian and Orthogonal matrices are always diagonalizable.

1.5.4 Hilbertspaces and Operators

As we promised, it turns out "the space of all functions f(x) with certain properties", is also a vector space. For these properties we shall take that $\int dx|f(x)|^2 < \infty$, which is called $\mathbb{L}_2$ the set of all square integrable functions.

The mathematically minded can see that functions are also "vectors" by ticking off the definitions of a vector space in section 1.5.3 one by one (exercise, see also Griffith section 3.2). A more intuitive way to understand why functions can be treated as vectors is to discretize the space they are defined on as in the figure below. You would have to do this anyway, whenever you want to handle functions with a computer.



left: A continuous real function $f(x)$ (blue) of one real number can be discretised by allowing only certain input values x_n with integer index n, and thus requiring function values at those points only $f_n = f(x_n)$. When we make the spacing $\Delta x = |x_{n+1} - x_n|$ between adjacent discrete points infinitely small, we recover the continuous function.

Once discretized, we can represent the function $f(x)$ as a vector $\mathbf{f} = [f_1, f_2, f_3, \cdots, f_n, f_{n+1} \cdots]^T$ just as in section 1.5.3. However, since we formally would need to define infinitely many points x_k to cover $-\infty < x < \infty$, this is an infinite dimensional vector. The advantage of realizing that e.g. $\mathbb{L}_2$ forms a vector space, is that we can generalize all the other useful concepts of section 1.5.3 to functions as well, as we shall do in the following.

We start with the scalar product $\mathbf{v} \cdot \mathbf{u}$, where we can instead use a

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[6] but not all, see linear algebra

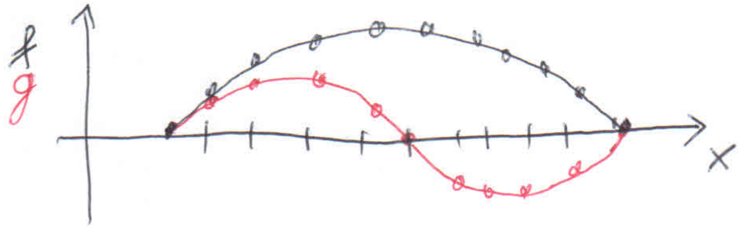
Scalar product of functions. Consider two functions in $\mathbb{L}_2$: $f(x)$, $g(x)$. We take

$$(f, g) = \int_{-\infty}^{\infty} dx f^*(x) g(x) \tag{1.17}$$

as their scalar product.

- Mathematically one can again use a formal definition of the properties of a scalar product, which $\mathbf{v} \cdot \mathbf{u}$ and (f, g) both fulfill, see linear-algebra books.
- Using the function scalar product, we can mostly importantly directly define the norm of a function $||f|| = (f, f) = \int_{-\infty}^{\infty} dx |f(x)|^2$, in direct analogy to the norm of a vector $\mathbf{v} \cdot \mathbf{v}$. We then also call two functions f and g orthogonal, if $(f, g) = 0$.

Example 8, Discretized orthogonal functions: Consider the two (real) functions below, for which we also indicate a possible discretisation.



left: Two real functions f (black) and g (red), with their discretisation •

Since the integration $(f, g) = \int_{-\infty}^{\infty} dx f^*(x) g(x) \equiv I$ is originally anyway defined via the discrete sum $I = \sum_n \Delta x f_n^* g_n$, we can see that this is directly proportional to a vector scalar product. We can also see how these two functions are orthogonal, since each possible product $f_n^* g_n$ is compensated by one other term of opposite sign.

We can combine both prior concepts and define the

Hilbert space: as a complete[a] vector space with a certain scalar product.

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[a] See math books, not so crucial here

- The primary example here is $\mathbb{L}_2$ with the scalar product (1.17).
- We later see that all quantum wavefunctions form what we call the Hilbert-space in this lecture. This will be enough for chapter 2 of this lecture. Later, in chapter 3, we introduce even more abstract Hilbert spaces.

Since it is a vector space, also the Hilbert space $\mathbb{L}_2$ has a basis:

Function space basis: We can write every function $f(x)$ in $\mathbb{L}_2$ in terms of an infinite dimensional basis $\{b_n(x)\}$, such that

$$f(x) = \sum_{n=0}^{\infty} f_n b_n(x). \tag{1.18}$$

If the basis $b_n(x)$ is orthonormal, which means $(b_n(x), b_m(x)) = \delta_{nm}$, we can find the expansion coefficients as $f_n = (b_n, f)$ (exercise).

- As for column vector-space bases, there are many different bases.

Example 9, Function space bases: A basis that you have already seen in other courses, is the basis of polynomials, which is used in the Taylor expansion:

$$f(x) = \sum_{n=0}^{\infty} \underbrace{\left(\frac{f^{(n)}(0)}{n!}\right)}_{=f_n} \underbrace{x^n}_{=b_n(x)}. \tag{1.19}$$

Another one is used in the Fourier series for even functions with period L (See PHY106, section 2.3.2):

$$f(x) = \sum_{n=0}^{\infty} \tilde{f}_n \cos\left(\frac{2\pi n}{L} x\right). \tag{1.20}$$

Both bases have the cosmetic drawback that the basis elements themselves are not in $\mathbb{L}_2$ and they hence span a *too large* space. We will see many more examples of bases without this problem later in this course.

Next, we want to generalize the concept of a matrix (or linear transformation) to function vector spaces. We use the

Linear operator: as a linear map $O : \mathbb{L}_2 \to \mathbb{L}_2$ of one function onto another, i.e.

$$\hat{O} f(x) = g(x). \tag{1.21}$$

We say in (1.21) the operator $\hat{O}$ is applied onto the function $f(x)$ to yield the function $g(x)$.

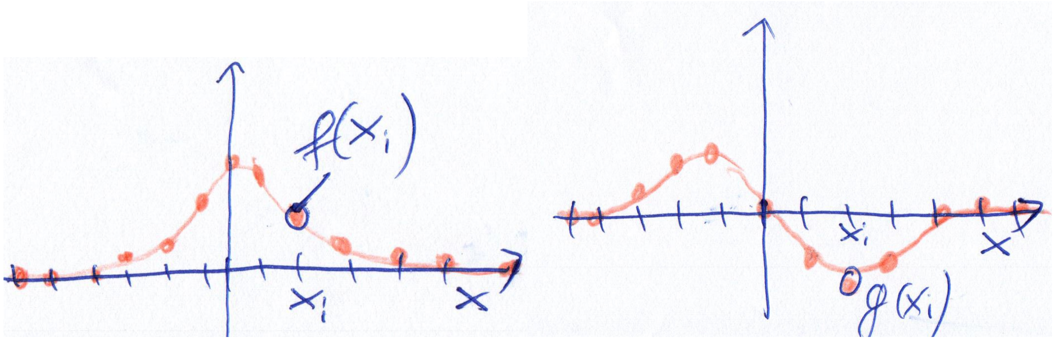
- It is often helpful when doing quantum mechanics, to denote all operators with hats to distinguish them from the variables they describe (eigenvalues, see below). We shall consistently use the hat in this lecture.
- Note that (1.21) is structurally equivalent to a matrix-vector multiplication $\underline{\underline{M}}\mathbf{v} = \mathbf{w}$ or the linear map (1.11) (in fact it IS a linear map, in the vector space of functions).

- Griffith calls Operators also “linear transformations”, but many other books call them operators.

To once again understand the relation between matrices and operators through a discretisation of space, see this example

Example 10, Differential operator as a matrix: A simple example is the derivative operator $\hat{O} \to \frac{\partial}{\partial x}$. Then, for example $\hat{O}\,\underbrace{e^{-x^2}}_{=f(x)} = \underbrace{-2xe^{-x^2}}_{=g(x)}$.

Both functions are drawn below in a discretized form as used in example 1.5.4.



First we can write each function as a vector $\mathbf{f} = [f(x_1), f(x_2), \cdots, f(x_n), \cdots]^T$, $\mathbf{g} = [g(x_1), g(x_2), \cdots, g(x_n), \cdots]^T$. We recall (one possible) definition of a derivative $f'(x) = \lim_{\Delta x \to 0}[f(x+\Delta x) - f(x-\Delta x)]/(2\Delta x)$, but use it without the limit $\Delta x \to 0$, for a small but finite $\Delta x = x_2 - x_1$. You can convince yourself that it is then possible to write a matrix

$$\underline{\underline{Q}} = \frac{1}{2\Delta x}\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & \\ -1 & 0 & 1 & 0 & 0 & 0 & \\ 0 & -1 & 0 & 1 & 0 & 0 & \cdots \\ 0 & 0 & -1 & 0 & 1 & 0 & \\ 0 & 0 & 0 & -1 & 0 & 1 & \\ 0 & 0 & 0 & 0 & -1 & 0 & \\ & & & \vdots & & & \end{bmatrix}, \tag{1.22}$$

such that $\mathbf{g} = \underline{\underline{Q}} \cdot \mathbf{f}$. We call $\underline{\underline{Q}}$ a matrix representation of the operator $\hat{O}$.

We will see later (in section 3) that in quantum mechanics indeed any operator can be represented by a matrix.

At this point we can write the

Operator eigenvalue equation:

$$\hat{O} f_n(x) = o_n f_n(x), \tag{1.23}$$

for a linear operator $\hat{O}$, and eigenvalues o_n for eigenfunction $f_n(x)$.

- An example would be $\underbrace{\frac{\partial}{\partial x}}_{=\hat{O}} \underbrace{\exp[kx]}_{=f_k(x)} = \underbrace{k}_{=\lambda_k} \exp[kx]$.

Due to the analogy between matrices and operators discussed in example 10, all names for matrices that we introduced earlier generalize also for operators. In particular we require the notion of a

Hermitian operator as an operator $\hat{O}$ for which

$$\left(\int_{-\infty}^{\infty} dx\, f^*(x) \hat{O} g(x) \right)^* = \int_{-\infty}^{\infty} dx\, g^*(x) \hat{O} f(x). \tag{1.24}$$

- Note, the definition makes use of the scalar product (1.17) between $f(x)$ and $\hat{O}g(x)$.
- An example that you met in PHY106 (week 8), is $\hat{O} = -i\hbar\frac{\partial}{\partial x}$. Note, without the i it would not be Hermitian.

We now have at last reached the point which we wanted to deliver before week 2, that is the

Eigenfunctions of a Hermitian operator form an orthonormal basis of the Hilbertspace. Let $\hat{O} f_n(x) = o_n f_n(x)$. That the $f_n(x)$ form a basis means that we can write any arbitrary function $g(x)$ as

$$g(x) = \sum_{n=0}^{\infty} g_n f_n(x), \tag{1.25}$$

for some suitable coefficients $g_n \in \mathbb{C}$. That the $f_n(x)$ are orthonormal implies

$$(f_n, f_k) = \int dx\, f_n^*(x) f_k(x) = \delta_{nk} \tag{1.26}$$

- We will prove this statement in week 6 and discuss this much more.
- Being able to make the statement above was the reason that we preponed some element from Griffith chapter 3. It is possible to understand most of the material from weeks 2-5 also without it, and they will provide many illustrative examples. Hence if the last parts of this week have confused you, don't worry for now, but please revisit this after week 6.

The above is a lot of material for one " week", however I assume that the elements on complex numbers, vectors, matrices and probability theory are mostly familiar to you. Wherever it was not, it is crucial that you revise this from other sources. In practice, quantum mechanics very heavily requires linear algebra and probability theory. For the part of the week above starting from section 1.5.4 (which the mathematicians call "functional analysis"), I do NOT assume that you knew it before. Hence, if that was too fast, please ask plenty of questions.

Week ②

PHY 303 Quantum Mechanics

Instructor: Sebastian Wüster, IISER Bhopal, 2023

These notes are provided for the students of the class above only. There is no guarantee for correctness, please contact me if you spot a mistake.

1.6 The basic structure of quantum mechanics

Armed with the mathematical framework that we developed in section 1.5, we shall now revisit the essential structure of quantum mechanics that you already learnt in PHY106, also deepening the math level. Later we will do a second step of deepening the math content in section 3. There will not be many examples in this section, since the following weeks provide many.

1.6.1 Normalisation and phase of wavefunctions

We already reviewed in section 1.4 that the quantum state of a particle is given by a complex wave function $\Psi(x,t)$ that is a solution of the TDSE (1.2). Importantly, (1.2) is linear, which means that (i) if we have one solution $\Psi(x,t)$ then $\Psi_c(x,t) = c\Psi(x,t)$ is also a solution, for an arbitrary complex number c, and (ii) If we found two solutions $\Psi_1(x,t)$ and $\Psi_2(x,t)$, then also $\Psi_3(x,t) = c_1\Psi_1(x,t) + c_2\Psi_2(x,t)$ is a solution. The latter is called the superposition principle, and holds for any linear wave equation (see also PHY106).

We can use property (i), to always make sure of

Wavefunction normalisation Since we know that $|\Psi(x,t)|^2 dx$ ought to be the probability at time t to find the particle between x and $x + dx$ (for infinitesimal dx), and the total probability has to be unity (see section 1.5.2), we require:

$$\int_{-\infty}^{\infty} dx\, |\Psi(x,t)|^2 = 1. \tag{1.27}$$

- Due to property (i) above, if we have any wavefunction $\tilde{\Psi}$ in $\mathbb{L}_2$ solving the TDSE that is not normalised to one, say instead $\int_{-\infty}^{\infty} dx\, |\tilde{\Psi}(x,t)|^2 = A$, then we know also $\Psi(x,t) = \tilde{\Psi}(x,t)/\sqrt{A}$ is a solution, and this one IS normalized to one (mini exercise).
- For physical quantum states, we should only ever consider states in $\mathbb{L}_2$ for which this procedure is possible.
- However we will later see (and have already seen in PHY106), that it is sometimes useful for math, and instructive for physics to also consider states that are non-normalizable for

$-\infty < x < \infty$ (these are thus not part of $\mathbb{L}_2$). The most important example is the infinite plane wave $\exp[ikx]$, for which $A \to \infty$. We will see some tricks on how to handle those functions anyway in section 2.1.

- You can show as a relative simply but instructive exercise, or read up in Griffith, that if at any given time t the wavefunction is normalized, the TDSE (1.2) ensures that it also remains normalized for all later times $t' > t$. This is also called conservation of probability.

Let us write the complex factor c form above in polar notation as $c = re^{i\varphi}$, with amplitude $r \in \mathbb{R}$ and phase φ. We see that the normalisation condition (1.27) fixes r but not φ. For a quantum state, its so-called global phase is thus undefined. Later we see that φ is not physically relevant (cannot be measured).

1.6.2 Momentum and other operators

While the state of a particle becomes a wavefunction in quantum mechanics, observables dependent on this state are represented by operators, introduced in section 1.5.4. The reason is ultimately that we need a mathematical formalism that gives rise to Heisenberg's uncertainty principle (see PHY106, week6), which is observed in nature. We shall see in section 3 why observables thus have to be operators, and what precisely is meant by "represented by...".

The simplest operator is the position operator, which is just the multiplication by x, i.e. $\hat{x}\Psi(x,t) = x\Psi(x,t)$. Since we already know that $|\Psi(x,t)|^2$ it the position space probability density of the particle, we can use the basic definition Eq. (1.6) and write the

Expectation value of position

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} dx\, x|\Psi(x,t)|^2 = \int_{-\infty}^{\infty} dx\ \Psi^*(x,t)\hat{x}\Psi(x,t) \tag{1.28}$$

- We shall see shortly that for expectation values of an operator, the operator has to be sandwiched between the wave functions. Of course once we realize that in the case of the position operator, the operation is merely a multiplication, this no longer matters. For other operators it DOES matter.

- Be careful about the name "expectation value". It does not mean the expected outcome of a measurement of position. Neither does it even have to be one of the possible outcomes of a measurement of position. It instead means the expected (and then indeed certain) average of a very large number of measurements of positions of particles that are identically prepared, such that they are described by the wavefunction Ψ. Again, not repeated measurements of the position of the same particle.

- Importantly, the expectation value thus makes reference to the wavefunction $\Psi(x,t)$. It of course be different for different wavefunctions.

We had already seen arguments in PHY106, how one is lead to the

Momentum operator in one dimension

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}. \tag{1.29}$$

- In PHY106 week8, we saw how this can extract information about the momentum since the latter is encoded in the wavelength or wavenumber of $\Psi(x,t)$, and the wavenumber k in a plane-wave e^{ikx} is appearing as multiplication after applying the momentum operator.
- We will still use the 1D version (1.30) for a while, but for completeness already mention the 3D momentum operator

  $$\hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}. \tag{1.30}$$

  Note, that this is now a vector of operators or vectoroperator, $\hat{\mathbf{p}} = -i\hbar[\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial x}]^T$. Its application onto a wavefunction will again be a vector.

To see another line of thought that motivates the choice (1.30) for the momentum operator, consider the rate of change of a position expectation value:

$$\frac{\partial}{\partial t}\langle x\rangle = \frac{\partial}{\partial t}\int_{-\infty}^{\infty} dx\ \Psi^*(x,t)x\Psi(x,t) = \cdots . \tag{1.31}$$

A common trick in derivations like this, is to exchange the order of differentiation and integration for two different variables[7]. We can then use the product rule inside the integrand

$$\cdots = \int_{-\infty}^{\infty} dx\left[\left(\frac{\partial}{\partial t}\Psi^*(x,t)\right)x\Psi(x,t) + \Psi^*(x,t)x\left(\frac{\partial}{\partial t}\Psi(x,t)\right)\right] \tag{1.32}$$

$$\overset{Eq.\ (1.2)}{=} \int_{-\infty}^{\infty} dx\Bigg[\left(\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\frac{\Psi^*(x,t)}{-i\hbar}\right)x\Psi(x,t) + \Psi^*(x,t)x\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\frac{\Psi(x,t)}{i\hbar}\Bigg].$$

For the left part of the last line, we had to first take the complex conjugate of Eq. (1.2), in order to get an equation involving $\Psi^*(x,t)$. We see that the terms involving the potential $V(x)$ cancel and the rest becomes

$$\cdots = -\frac{i\hbar^2}{2m}\int_{-\infty}^{\infty} dx\, x\underbrace{\left[\left(\frac{\partial^2}{\partial x^2}\Psi^*(x,t)\right)\Psi(x,t) - \Psi^*(x,t)\left(\frac{\partial^2}{\partial x^2}\Psi(x,t)\right)\right]}_{=\frac{\partial}{\partial x}\left(\frac{\partial\Psi^*(x,t)}{\partial x}\Psi(x,t) - \Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}\right)}. \tag{1.33}$$

We can now do integration by parts to "shift the $\partial/\partial x$ onto the x". We should get an additional boundary term $x\left(\frac{\partial\Psi^*(x,t)}{\partial x}\Psi(x,t) - \Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}\right)\Big|_{-\infty}^{\infty}$, but this has to vanish since $\lim_{x\to 0}\Psi(x,t) =$

---

[7] Mathematicians allow you this only for integrands that are "sufficiently nice", but this will usually be the case in physics.

0, if $\Psi(x,t)$ is supposed to be normalized as in (1.27). After than and one more integration by parts, we finally reach

$$\frac{\partial}{\partial t}\langle x\rangle = -\frac{i\hbar}{m}\int_{-\infty}^{\infty} dx\, \Psi^*(x,t)\frac{\partial}{\partial x}\Psi(x,t) = \langle \hat{p}/m\rangle. \tag{1.34}$$

For our earlier definition of $\hat{p}$, the rate of change of the position expectation value is thus the velocity expectation value, which seems to make sense.

After we applied the definitions of expectation values from section 1.5.2 to quantum mechanical operators, we can do the same for the standard deviations, to define:

Position and momentum uncertainties in the state $\Psi(x,t)$:

$$\text{Position uncertainty: } \sigma_x = \sqrt{\langle \hat{x}^2\rangle - \langle \hat{x}\rangle^2}, \tag{1.35}$$

$$\text{Momentum uncertainty: } \sigma_p = \sqrt{\langle \hat{p}^2\rangle - \langle \hat{p}\rangle^2}. \tag{1.36}$$

This is defined in analogy to (1.8).

Luckily all other physical observables in mechanics can be expressed in terms of position and momentum. Hence also the corresponding operators can be written accordingly in terms of the position and momentum operator. For example

Mechanical observables

$$\text{Kinetic energy:} \quad \hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, \tag{1.37}$$

$$\text{Potential energy:} \quad \hat{V} = V(\hat{x}), \tag{1.38}$$

$$\text{Total energy:} \quad \hat{H} = \hat{T} + \hat{V}, \tag{1.39}$$

$$\text{Angular momentum:} \quad \hat{L} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}. \tag{1.40}$$

- The total energy operator get special name, the Hamiltonian, in association with the "Hamiltonian function $H = \frac{p^2}{2m} + V(x)$ in classical mechanics (PHY305). We also recognize this as the operator on the RHS of Schrödinger's equation (1.2), which we could thus write as $i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}\Psi(x,t)$.
- We can see that all operators in the list above are Hermitian per (1.24) (exercise, use integration by parts).
- For any of the above operators $\hat{O}(\hat{x},\hat{p})$ the expectation value is then found as

$$\langle \hat{O}\rangle = \int_{-\infty}^{\infty} dx\, \Psi^*(x,t)O(x, -i\hbar\frac{\partial}{\partial x})\Psi(x,t), \tag{1.41}$$

  and its uncertainty via

$$\sigma_O = \sqrt{\langle \hat{O}^2\rangle - \langle \hat{O}\rangle^2}. \tag{1.42}$$

While particularly the appearance of the momentum operator as a derivative wrt. x makes all the above look very different from classical mechanics, it still contains much of the same gist, as we had shown you from a simulation in example 1. We can also analytically see this in

Example 11, Ehrenfest's theorem: The expectation values of position and momentum are linked as in classical physics[a], i.e. Eq. (1.34) and

$$\frac{\partial}{\partial t}\langle\hat{p}\rangle = -\langle\frac{\partial}{\partial x}V(x)\rangle. \tag{1.43}$$

Proof: Exercise, follow similar steps as for Eq. (1.34). Together with that equation:

$$\frac{\partial}{\partial t}\langle x\rangle = \langle\hat{p}/m\rangle. \tag{1.44}$$

this forms Ehrenfest's theorem, stating that the quantum mechanical expectation values evolve as in classical mechanics. Note, that Ehrenfest's theorem does not tell us how uncertainties evolve, only averages. Since in the initial times of example 1 uncertainties are small, the mean and center position remain almost at the same place, hence the theorem explains why the support region of the probability density just follows Newton's equations.

---

[a] Via Hamilton's equations, see PHY305.

1.6.3 Heisenberg's uncertainty principle

We know from PHY106, that the momentum is encoded in a wavefunction $\Psi(x,t)$ through its wavelength. The specific link is given by the

De-Broglie wavelength

$$\lambda_{\mathrm{dB}} = \frac{h}{p}, \tag{1.45}$$

where h is Planck's constant (1.3) and $p = |\mathbf{p}|$ the momentum (modulus).

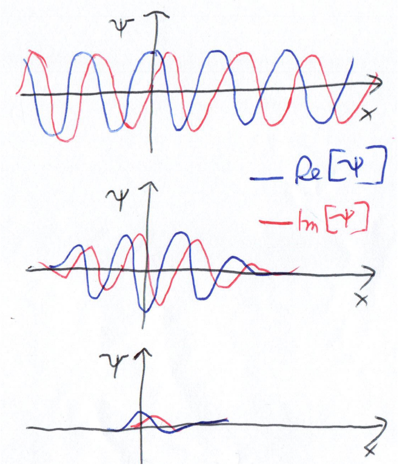
- In one dimension an example of a wavefunction with a well defined momentum p is $\Psi(x) = e^{i\frac{p}{\hbar}x}/\sqrt{(}V)$ (but see section 1.6.1 regarding normalisation issues).
- With the usual conversion from wavelength to wavenumber $\mathbf{k}$, we can also write

  $$\mathbf{p} = \hbar\mathbf{k}. \tag{1.46}$$

  Note these are now 3D vectors. The 3D wavevector $\mathbf{k} = [k_x, k_y, k_z]^T$ defines a planewave $\Psi(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}}/\sqrt{V}$.

We had discussed at some length in PHY106 week6, that there is a tradeoff between how well we know the wavelength of some wavefunction versus how well we know its "position":

Example 12, Wave localisation versus wavelength:



left: Three examples of complex wavefunctions with differently strong spatial localisation, and differently well defined wavelength. (top) Plane wave $\sim e^{ikx}$ has a perfectly well defined wavelength, but no localisation. (middle) A wavepacket is somewhat localized, but we saw in PHY106 and will see more formally later, how this comes at a tradeoff of some spread in wavelengths. (bottom) Sub-cycle wave: Here it becomes very difficult to even read off any wavelength.

This tradeoff gives rise to

Heisenberg's uncertainty principle (HUP)

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}, \tag{1.47}$$

for the position uncertainty σ_x and momentum uncertainty σ_p defined in Eq. (1.35)-(1.36).

- For now we just remind you that you have seen this in PHY106. This time we shall formally prove it in week 6, based on operator algebra (see section 1.5.4). We will then also generalize the HUP to other operators than position and momentum.
- Let us repeat that the HUP has nothing to do with imperfections in the position and momentum measurement apparatuses. It represents a fundamental limitation in simultaneously knowing position and momentum of a particle, which arises immediately once we realize that the particle must be described by a wavefunction.

1.6.4 Probability currents

The complex wave function $\Psi(x,t)$ can always be expressed through to real functions using the polar representation

$$\Psi(x,t) = \sqrt{\rho(x,t)} e^{i\varphi(x,t)}. \tag{1.48}$$

We already know to interpret $\rho(x,t) = |\Psi(x,t)|^2$ as local probability density. Let us clarify a bit further the meaning of the complex phase $\varphi(x,t)$. Inserting (1.48) into the TDSE (1.2) we can write:

$$
\begin{aligned}
&i\hbar\Big[\dot\rho(x,t)\frac{1}{2\sqrt{\rho(x,t)}}e^{i\varphi(x,t)}+i\dot\varphi(x,t)\sqrt{\rho(x,t)}e^{i\varphi(x,t)}\Big]\\
&=-\frac{\hbar^2}{2m}\bigg(\frac{\rho''(x,t)}{2\sqrt{\rho(x,t)}}+i\sqrt{\rho(x,t)}\varphi''(x,t)-\sqrt{\rho(x,t)}\varphi'(x,t)^2+i\frac{\rho(x,t)'\varphi'(x,t)}{\sqrt{\rho(x,t)}}\\
&-\frac{\rho(x,t)'^2}{4\rho(x,t)^{3/2}}\bigg)e^{i\varphi(x,t)}+V(x)\sqrt{\rho(x,t)}e^{i\varphi(x,t)}. \qquad (1.49)
\end{aligned}
$$

We have used the notation $\frac{\partial^2}{\partial x^2}f(x)=f''$ and otherwise just used the chain and product rules for differentiation. At this point we can divide both sides by $e^{i\varphi(x,t)}$ and then separately equate the real and imaginary parts of the left and right hand sides, since all variables are now real. This yields:

$$
-\hbar\dot\varphi(x,t)\sqrt{\rho(x,t)}=-\frac{\hbar^2}{2m}\bigg(\frac{\rho''(x,t)}{2\sqrt{\rho(x,t)}}-\sqrt{\rho(x,t)}\varphi'(x,t)^2-\frac{\rho'(x,t)^2}{4\rho(x,t)^{3/2}}\bigg)+V(x)\sqrt{\rho(x,t)}, \qquad (1.50)
$$

$$
\hbar\dot\rho(x,t)\frac{1}{2\sqrt{\rho(x,t)}}=-\frac{\hbar^2}{2m}\bigg(\sqrt{\rho(x,t)}\varphi''(x,t)+\frac{\rho'(x,t)\varphi'(x,t)}{\sqrt{\rho(x,t)}}\bigg). \qquad (1.51)
$$

We multiply Eq. (1.50) by $-(\hbar\sqrt{\rho(x,t)})^{-1}$ and Eq. (1.51) by $2\sqrt{\rho(x,t)}/\hbar$ to reach

$$
\dot\varphi(x,t)=-\frac{\hbar}{2m}\bigg(\frac{\rho''(x,t)}{2\rho(x,t)}+\varphi'(x,t)^2+\frac{\rho'(x,t)^2}{4\rho(x,t)^2}\bigg)-V(x)/\hbar, \qquad (1.52)
$$

$$
\dot\rho(x,t)=-\frac{\hbar}{m}\bigg(\rho(x,t)\varphi''(x,t)+\rho'(x,t)\varphi'(x,t)\bigg)=-J'(x,t), \qquad (1.53)
$$

where we have used the

Probability current for a wavefunction $\Psi(x,t)$ is

$$
J(x,t)=\frac{i\hbar}{2m}\left[\Psi\frac{\partial\Psi^*}{\partial x}-\Psi^*\frac{\partial\Psi}{\partial x}\right]=\frac{\hbar}{m}\mathfrak{Im}\left[\Psi^*\frac{\partial\Psi}{\partial x}\right]=\frac{\hbar}{m}\rho(x,t)\frac{\partial\varphi(x,t)}{\partial x} \qquad (1.54)
$$

The second equation, (1.53), takes the form of a continuity equation involving the probability density and probability current, just like we would have e.g. in hydrodynamics for the particle density and particle current.[8].

Integrating the LHS of (1.53) over $\int_a^b dx\cdots$, we can write for the total probability in the interval $[ab]$ that

$$
\dot P_{ab}=J(a)-J(b), \qquad (1.55)
$$

see section 1.5.2, i.e. the total probability in that interval changes according to the difference of the ingoing and outgoing probability current.

---

[8] We can even write Eq. (1.52) in a form similar to Bernoulli's equation in hydrodynamics, but now involving a so-called quantum pressure

1.6.5 Stationary states

So far, we have spent most of this section with a general discussion of quantum mechanical principles. In the next section we want to finally start solving stuff and seeing real examples. Solving the TDSE (1.2) analytically is not possibly in all cases. Particularly note that this is a partial differential equation (PDE), containing partial derivatives with respect to at least two variables, x and t.

A huge simplification is possible, whenever the Hamiltonian $\hat{H}$ in (1.39) does not explicitly depend on time. This would for example be true for a plain harmonic oscillator potential $V(x) = \frac{1}{2}m\omega^2 x^2$, but not the driven oscillator potential $V(x,t) = \frac{1}{2}m\omega^2(x - x_0\cos[\omega t])^2$. Note that we are talking about the potential energy function $V(x)$ in the Hamiltonian, not the actual potential energy of the particle, which is $\langle V(x)\rangle = \int dx \Psi^*(x,t)V(x)\Psi(x,t)$. The latter may be time dependent even if $V(x)$ is not.

For a time-independent Hamiltonian, we can tackle the TDSE with

Separation of variables: This is a trick to reduce the complexity of PDEs. Consider a generic PDE for a function $f(a,b)$ of two variables a, b

$$P\left[a, \frac{\partial}{\partial a}, b, \frac{\partial}{\partial b}, f(a,b)\right] = 0. \tag{1.56}$$

We make the attempt to write the solution as a product $f(a,b) = g(a)h(b)$ of two functions that depend only on one variable, and insert this into (1.56).
We then attempt to segregate everything that depends on a on the LHS and everything that depends on b on the RHS to write

$$P_1\left[a, \frac{\partial}{\partial a}, g(a)\right] = P_2\left[b, \frac{\partial}{\partial b}, g(b)\right], \tag{1.57}$$

we conclude that *both sides have to be equal to the same constant*:

$$P_1\left[a, \frac{\partial}{\partial a}, g(a)\right] = const = P_2\left[b, \frac{\partial}{\partial b}, g(b)\right]. \tag{1.58}$$

We can now solve the two equations obtained separately, which is much easier since they each involve *only one variable.*

- Proof: The LHS will overall be a function of a, and the RHS of b. The equation (1.57) implies that LHS=RHS for all possible combinations of values for a and b. Suppose the equation is correct for some values a_0, b_0 hence $LHS(a_0) = RHS(b_0)$, if either of them was not constant (say RHS), we can find another value $b \neq b_0$ such that $RHS(b_0) \neq RHS(b)$, hence also $LHS(a_0) \neq RHS(b)$, which proves the assertion by contradiction.

- We only discussed the case of two variables above, but it may work also for many. In that case we first "separate off" one of them as above (bring it to LHS and all others to the RHS). We then repeat the process with the equation we reached for the RHS. We shall see an example in chapter (4), dealing with the Hydrogen atom.

- In the box above we mentioned "attempt to" many times: The procedure of course *does not work* for most PDEs. If it does, we are lucky.
- IF it does work however, we typically know that we have found ALL solutions, despite the apparent restrictiveness of our "guess" $f(a,b) = g(a)h(b)$. This is due to some theorem the mathematicians can provide that tells us how many different solutions a certain PDE can have. In our cases, it will mean IF the guess works, it is ALL the solutions.

Let us now apply "Separation of variables" to the TDSE for the case of a time-independent Hamiltonian, which will also serve as a practical example. We make the Ansatz $\Psi(x,t) = \phi(x)c(t)$ as in the box above ($a \to x$, $b \to t$), insert this into (1.2) and apply derivatives, to find:

$$i\hbar\phi(x)\frac{\partial}{\partial t}c(t) = -\frac{\hbar^2}{2m}c(t)\frac{\partial^2}{\partial x^2}\phi(x) + V(x)\phi(x)c(t). \tag{1.59}$$

We now divide both sides by $\phi(x)c(t)$:

$$i\hbar\frac{\frac{\partial}{\partial t}c(t)}{c(t)} = -\frac{\hbar^2}{2m}\frac{\frac{\partial^2}{\partial x^2}\phi(x)}{\phi(x)} + V(x). \tag{1.60}$$

At this point we have reached the form (1.57) where all time dependence is on the left and all space dependence on the right. LHS and RHS thus have to be equal to the same constant. We call that constant E, and re-write the two resultant equations as:

$$i\hbar\frac{\partial}{\partial t}c(t) = Ec(t), \tag{1.61}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi(x) + V(x)\phi(x) = E\phi(x). \tag{1.62}$$

We have now turned the PDE (1.2) into two *ordinary differential equations* (ODEs). The first one (1.61) is easy to solve as $c(t) = c(0)e^{-iEt/\hbar}$. Since we care only about the product $\phi(x)c(t)$ later, we can absorb $c(0)$ into $\phi(x)$ and write $c(t) = e^{-iEt/\hbar}$ for now. The second equation is called

Time-independent Schrödinger equation (TISE) for the Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\phi_n(x) = \hat{H}\phi_n(x) = E_n\phi_n(x). \tag{1.63}$$

- Note that we have added the subscript n to $\phi(x)$ in Eq. (1.63), to indicate that an equation of type (1.63) typically has many solutions, as you have already seen in PHY106 (weeks 8 and 9). Often we can take these as countably infinite, then we use an integer $n \in \mathbb{Z}$. They can also be uncountably infinite, so we should better use a real label k to distinguish different solutions $\phi(k,x)$.

(i) **Solutions $\phi(x)$ of the TISE are stationary states:** The complete wave function $\phi(x)e^{-iEt/\hbar}$ does depend on time, however in such a way that the probability density $\rho(x)$ does not:

$$\rho(x,t) = |\Psi(x,t)|^2 = \Psi^*(x,t)\Psi(x,t) = \phi^*(x)e^{iEt/\hbar}\phi(x)e^{-iEt/\hbar} = |\phi(x)|^2 \equiv \rho(x). \tag{1.64}$$

The same will be true for the expectation value (see Eq. (1.41)) of any operator (exercise).

(ii) **Solutions $\phi_n(x)$ of the TISE have a definite energy:** We had seen in section 1.6.2 that the total energy is represented by the Hamiltonian $\hat{H}$. For its expectation value in the state $\phi_n(x)$ we can thus write

$$\langle \hat{H} \rangle = \int dx\, \phi_n^*(x)\hat{H}\phi_n(x) \overset{Eq.\ (1.63)}{=} \int dx\, \phi_n^*(x)E_n\phi_n(x) = E_n \int dx\, |\phi_n(x)|^2 \overset{Eq.\ (1.27)}{=} E_n. \tag{1.65}$$

Similarly we can calculate the uncertainty using Eq. (1.42) and find $\sigma_H^2 = 0$ (exercise/Griffith). The state thus has energy E_n (which is why we used that letter to denote the constant arising in separation of variables) and that energy has no fluctuations (it is definite).

(iii) **The set of all solutions $\phi_n(x)$of the TISE also provides us with all solutions of the TDSE:** For this, we compare Eq. (1.63) with Eq. (1.23), to see that the TISE is the eigenvalue equation of the Hamiltonian, thus E_n are its eigenenergies and $\phi_n(x)$ the corresponding eigenfunctions. Since $\hat{H}$ is a Hermitian operator (see Eq. (1.24)), we know that all energies E_n have to be real and that the eigenfunctions $\phi_n(x)$ always form a complete orthonormal basis of the Hilbertspace, see Eq. (1.25). This is an extremely powerful statement, as we shall see now. Recall from the comment after Eq. (1.2), that the TDSE predicts the future wavefunction $\Psi(x, t > 0)$ from some initial state $\Psi(x, t = 0) \equiv \Psi_0(x)$. Since the $\phi_n(x)$ form a basis, we can expand the initial state as

$$\Psi_0(x) = \sum_n c_n(0)\phi_n(x), \tag{1.66}$$

for some *complex or real* coefficients $c_n(0)$. Due to the orthogonality Eq. (1.26) of the eigenfunctions $\phi_n(x)$, we can find these coefficients using:

$$c_k(0) = \int dx\, \phi_k^*(x)\Psi_0(x), \tag{1.67}$$

as you can show as an exercise. The same expansion must be possible at any later time, so we write

$$\Psi(x, t) = \sum_n c_n(t)\phi_n(x), \tag{1.68}$$

and insert this into the TDSE (1.2). We obtain

$$\begin{aligned} i\hbar \sum_n \dot{c}_n(t)\phi_n(x) &= \sum_n c_n(t) \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \right] \phi_n(x), \\ &\overset{Eq.\ (1.63)}{=} \sum_n c_n(t)E_n\phi_n(x). \end{aligned} \tag{1.69}$$

We now integrate both sides over $\int dx\phi_k^*(x)\cdots$. This is called "projecting the equation onto $\phi_k(x)$ and completely analogous to taking the scalar product $\mathbf{v} \cdot ...$ on both sides of a vector equation (this would be called "projecting onto $\mathbf{v}$"). Using again (1.26), this gives us (after dividing by $\phi_k(x)$):

$$i\hbar\dot{c}_k(t) = c_k(t)E_k, \tag{1.70}$$

which is solved by $c_k(t) = c_k(0)e^{-iE_k t/\hbar}$. We already know that $c_k(0)$ is given by Eq. (1.67), with $\Psi_0(x)$ assumed known. We thus reached the

General solution of the TDSE for a time-independent Hamiltonian:

$$\Psi(x,t) = \sum_n c_n(0)e^{-iE_n t/\hbar}\phi_n(x). \tag{1.71}$$

(iv) One warning: Solutions $\phi_n(x)$ of the TISE are always defined only up to an arbitrary complex number. Proof: Define $\chi_n(x) = z\phi_n(x)$ if $\phi_n(x)$ is a solution of (1.63) and you shall find that also $\chi_n(x)$ is a solution since the z remains on both sides of the equation. We can fix the magnitude of $\phi_n(x)$ by the requirement of normalisation (1.27). But not the complex phase. I.e every solution can always be multiplied with $e^{i\varphi}$ and remains a solution. In most of the next week, we choose solutions that are real, but we would not have to. In particular even for real functions, we can multiply them with $(-1) = e^{i\pi}$ if we want to.

We will come back to all statements in this week in the next few weeks, which serve as extensive example collection.

Week ③

PHY 303 Quantum Mechanics
Instructor: Sebastian Wüster, IISER Bhopal, 2023

These notes are provided for the students of the class above only. There is no guarantee for correctness, please contact me if you spot a mistake.

2 Solvable quantum problems in one dimension

We want to now apply our results on stationary states from section 1.6.5 to as many problems as possible and in doing so also understand how and why this tells us all we need to know about quantum mechanical problems. For simplicity we shall stick to a single spatial dimension x, i.e. working in 1D. We will see later (chapter 4), how to straightforwardly generalize most of these results to 3D. The problems in this section probably already almost exhaust the list of those where the quantum states and dynamics can be analytically found.

2.1 Free particle eigenstates

Let us first start to look at the simplest system, the free particle. Free particle means, that no force acts on the particle and hence the potential must be a constant $V(x) = V_0$. For simplicity V_0 is usually set to zero. We then have the

Free particle Hamiltonian, which is just $\hat{H} = \hat{p}^2/(2m)$, hence

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}. \tag{2.1}$$

This gives rise to the TISE

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi(x) = E\phi(x), \tag{2.2}$$

which we can write as

$$\frac{\partial^2}{\partial x^2}\phi(x) = -k^2\phi(x), \tag{2.3}$$

with constant $k = \sqrt{2mE}/\hbar$. You would have seen the differential equation (2.13) elsewhere, e.g. when dealing with the classical harmonic oscillator. Its general solution is $\phi(x) = A\sin[kx] + B\cos[kx]$, or equivalently $\phi(x) = Ce^{ikx} + De^{-ikx}$, linked though $C = B/2 + A/(2i)$ and $D = B/2 - A/(2i)$. In choosing one of the two forms, we shall be guided by something else we know about free particles: Their momentum should stay constant since they do not experience any force. We can see that the complex exponential function is a

Momentum eigenstate (plane wave solutions)

$$\phi(p,x) = \frac{1}{\sqrt{2\pi\hbar}} e^{i\frac{p}{\hbar}x} \tag{2.4}$$

with $\hat{p}\phi(p,x) = p\phi(p,x)$,

using Eq. (1.30). Hence we shall pick the second of the two ways to write the general solutions in terms of complex exponentials. A solution can be found for any energy $E > 0$, we call this a continuous spectrum of a Hamiltonian.

The states (2.4) have one draw-back, they cannot be normalized as in (1.27). Instead they have been chosen to fullfill the

Delta function normalisation

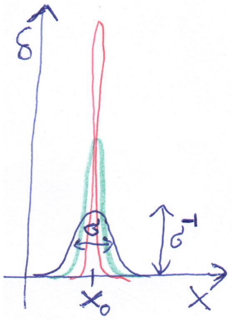
$$(\phi(p,x), \phi(p',x)) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dx\, e^{-i\frac{p}{\hbar}x} e^{i\frac{p'}{\hbar}x} = \delta(p-p'). \tag{2.5}$$

Here we made use of the

Dirac delta function: We define the object $\delta(x - x_0)$ such that

$$\int_{-\infty}^{\infty} dx\, f(x)\delta(x-x_0) = f(x_0), \tag{2.6}$$

for any test-function $f(x)$. In practice, you will ever only need Eq. (2.6).



left: You could loosely think of the delta-function as $= 0$ everywhere, except at x_0 where it is ∞. Clearly this definition is pathological. A better way is to think of it as the limit

$$\delta(x-x_0) = \lim_{\sigma\to 0} \frac{1}{\sqrt{\pi}\sigma} e^{-\frac{(x-x_0)^2}{\sigma^2}} \tag{2.7}$$

of an ever narrower Gaussian, as shown in the figure.

- The delta function is just a mathematical object, so its argument x can be any physical variable.
- Despite the name, the delta-function is not a genuine function, but mathematically a distribution or generalised function. That means we have to multiply it with a test-function and then integrate over it, to make sense of it, as we had seen above.
- The Delta function normalisation (2.5) now makes use of the important formula

$$(2\pi)\delta(x) = \int_{-\infty}^{\infty} dk\, e^{ikx}. \tag{2.8}$$

See Griffith page 59 for a refreshing discussion of this formula.

- An alternative normalisation also encountered is the box normalisation, where instead of an infinite space we assume (2.4) exists only within a volume $\mathcal{V}$ (in a 1D interval), we write $\phi(p,x) = \frac{1}{\sqrt{\mathcal{V}}} e^{i\frac{p}{\hbar}x}$ and then see that these are normalised according to (1.27).

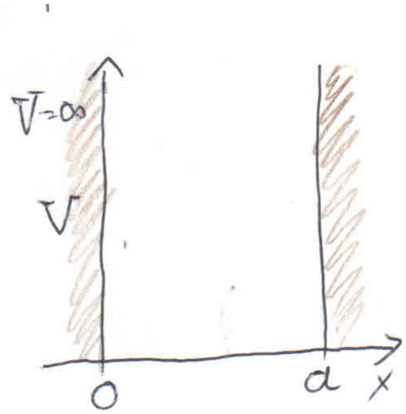
While the plane wave solutions (2.4) are straightforward to write down, the fact that they are not in the strict sense normalisable and form a continuous spectrum makes it harder to look at meaningful physics with them. We will thus defer a further discussion of the free particle to section 2.4, and first look at a few problems which are actually simpler to deal with, even though the Hamiltonian is seemingly more complicated.

2.2 Piecewise constant potentials

Just to group the problems logically, we will first consider potentials $V(x)$ that are piecewise constant, which is the next simpler setting compared to section 2.1. This means we can split space up at certain points x_k and write e.g.

$$\begin{aligned} &V(x) = V_- \text{ for } x \le x_0, \\ &V(x) = V_k \text{ for } x_k < x \le x_{k+1} \text{ with } k = 0, \cdots, N, \\ &V(x) = V_+ \text{ for } x > x_N. \end{aligned} \tag{2.9}$$

2.2.1 Infinite square well



left: We first consider the so-called infinite square well potential of width a, which is

$$\begin{aligned} &V(x) \to \infty \text{ for } x \le 0, \\ &V(x) = 0 \text{ for } 0 < x \le a, \\ &V(x) \to \infty \text{ for } x > a. \end{aligned} \tag{2.10}$$

If you are uncomfortable with the idea of an infinite potential, just set it to $V(x) = V_0$ outside the box, and then imagine the limit $V_0 \to \infty$.

Physically this implies the particle is free to move within $x = 0$ and $x = a$, but perfectly elastically reflects off the "walls" of that interval provided by the potential $V(x)$. We now want to solve the TISE (1.63) for this potential:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \right] \phi_n(x) = \hat{H}\phi(x) = E_n \phi_n(x). \tag{2.11}$$

to try and find all finite energy eigenvalues E_n.

- First note, that a differential equation such as (1.63) essentially gives you a condition “for every x”. That means we can first separately find its solution in each interval $x_k < x \leq x_{k+1}$ of (2.9).
- We have to then take special care of the connection points x_k, since the TISE contains a derivative and thus the condition does involve information from the adjacent intervals at these points.
- Finally, even if the potential was smooth, the TISE is of second order in x and thus will in general have infinitely many solutions even for the same energy E_n, given by adjusting two unknown (complex) constants A, B (math courses). These are fixed by the requirement of normalisation 1.27 and what is called the boundary conditions. Those tell us how the function $\phi_n(x)$ at the edge of the solution interval, typically for $x \to \pm\infty$. In the end we find a unique solution $\phi_n(x)$, up to a complex phase (see discussion in section 1.6.1) for the eigenfunction $\phi_n(x)$ belonging to the specific energy eigenvalue E_n. However there can still be infinitely many different pairs $(\phi_n(x), E_n)$.

We shall now follow this program for the infinite box potential to see what it means.

(i) We first note that outside the box, we require $\phi_n(x) \equiv 0$. Suppose that was not the case for some finite interval $[p_1 p_2]$ outside the box. If we then take the expectation value of potential energy, we see

$$\langle V(\hat{x}) \rangle \overset{Eq.\ (1.41)}{=} \int_{-\infty}^{\infty} dx\, V(x)|\phi_n(x)|^2 > \int_{p_1}^{p_2} dx\, \underbrace{V(x)}_{\to\infty} |\phi_n(x)|^2 \to \infty. \tag{2.12}$$

Since the total energy $E_n > \langle V(\hat{x}) \rangle$, it would be infinite, which does not make sense.

(ii) Inside the box, the TISE (2.11) can be written as before:

$$\frac{\partial^2}{\partial x^2}\phi_n(x) = -k_n^2 \phi_n(x), \tag{2.13}$$

with constant $k_n = \sqrt{2mE_n}/\hbar$. This time we write the general solution is $\phi_n(x) = A\sin[k_n x] + B\cos[k_n x]$, because a subsequent step will then be easier. Here you see how the two constants mentioned before come in. We can fix these using

Continuity conditions for wavefunctions (for solutions of the TISE): For all x at which the potential $V(x)$ has at most a finite jump, the wavefunction $\phi_n(x)$ and its derivative $\frac{\partial}{\partial x}\phi_n(x)$ must be continuous. At x where the potential $V(x)$ has a infinite jump, only the wavefunction $\phi_n(x)$ must be continuous, the derivative may be discontinuous.

Proof: We form the TISE into $\phi_n(x)'' = -2m[E_n - V(x)]\phi_n(x)/\hbar^2$ and integrate both the LHS and RHS as in $\int_{x_0-\epsilon}^{x_0+\epsilon} dx \cdots$ over a small interval adjacent to the point x_0, taken as $[x_0 - \epsilon, x_0 + \epsilon]$, with infinitesimal ϵ:

$$\int_{x_0-\epsilon}^{x_0+\epsilon} dx\, \phi_n(x)'' = \left[\phi_n(x_0+\epsilon)' - \phi_n(x_0-\epsilon)'\right] = -\frac{2m}{\hbar^2}\int_{x_0-\epsilon}^{x_0+\epsilon} dx\, \underbrace{[E_n - V(x)]\phi_n(x)}_{=I(x)}. \tag{2.14}$$

Taking the limit $\epsilon \to 0$, we see that as long as $V(x)$ was finite everywhere, the integrand $I(x)$ on the RHS is finite and thus $\lim_{\epsilon\to 0}\int_{x_0-\epsilon}^{x_0+\epsilon} dx I(x) = 0$. Then (2.14) implies that $\phi_n(x)'$ is continuous. If that is the case, we can redo a similar trick and write

$$\int_{x_0-\epsilon}^{x_0+\epsilon} dx\, \phi_n(x)' = \left[\phi_n(x_0+\epsilon) - \phi_n(x_0-\epsilon)\right], \tag{2.15}$$

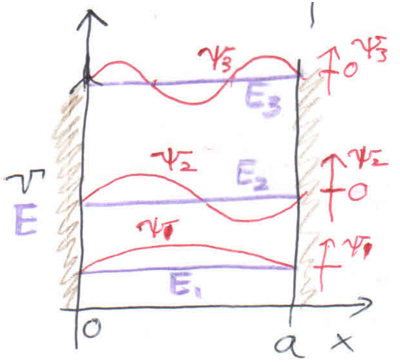
Again taking the limit $\epsilon \to 0$, we see that also $\phi_n(x)$ is continuous as long as $\phi_n(x)'$ is finite, which it is. If $V(x)$ is infinite or tends to infinite, the argument above does not hold, since we don't quite know what the RHS integral in (2.14) gives. We shall see an example later, where it can provide a finite answer and thus lead to a finite jump in the derivative $\phi_n(x)'$ at location x_0. However the wavefunction $\phi_n(x)$ itself always is continuous, even if the potential has an infinite jump.

(iii) We can now use the boundary conditions just derived to fix the constants A and B in the solution above. Since the wavefunction vanishes outside the box, it being continuous means

$$\begin{aligned} 0 &= \phi_n(0) = B, \\ 0 &= \phi_n(a) = A\sin[k_n a] + B\cos[k_n a]. \end{aligned} \tag{2.16}$$

We reached $\sin[k_n a] = 0$, which is the case for $k_n a = n\pi$, for integer n. We can see that $n = 0$ is not normalizable and $n < 0$ gives nothing new compared to $n > 0$, then we reach

Eigenstates and energies of the particle in the infinite square well



left: Drawing of energies E_n (violet), potential $V(x)$ (black) and wavefunctions (red, read $\Psi_n \to \phi_n$)

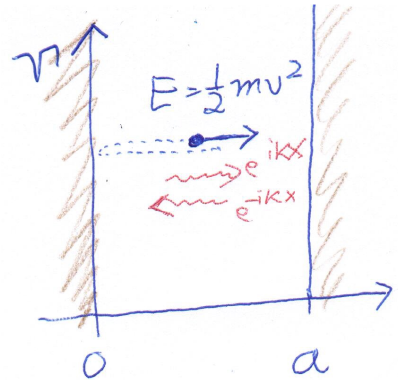
$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad \text{for } n = 1, 2, 3, \cdots \tag{2.17}$$

$$\phi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right). \tag{2.18}$$

- We have fixed the normalisation constant A through Eq. (1.27).
- There is an infinite number of solutions numbered by the quantum number n.
- Despite the crudeness of this potential, there is a lot of generally valid physics for quantum bound-states in it:
  (i) The smallest allowed energy E_1 is not zero.
  (ii) The stronger the confinement (lower a), the larger the energy spacing $E_{n+1} - E_n$.
  (iii) The higher the mass, the smaller the energy spacing $E_{n+1} - E_n$.

- Solutions alternate between symmetric and anti-symmetric with respect to the box centre. The number of their nodes is $n-1$. You can confirm that they are orthonormal (1.26) (exercise/Griffith), as expected from section 1.5.4, since the Hamiltonian is Hermitian.
- We also directly see that the eigenfunctions $\phi_n(x)$ form a basis of all functions in $[0,a]$, since $f(x)=\sum_n c_n\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$ (See Eq. (1.18)) is exactly the Fourier series.

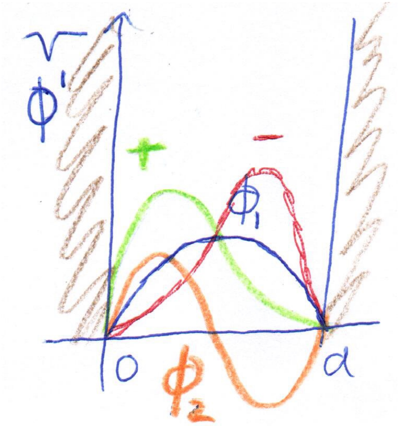
Example 13, Physical interpretation of particle in the box state:



left: Imagine what a classical particle in the box potential would do. Since there is no force between $[0,a]$ it would move there with constant velocity, only to experience a sudden elastic reflection when encountering the wall. It thus would bounce back and forth, with either momentum $p>0$ or $p<0$. As per our discussion in section 2.1, the corresponding momentum eigenstates are $e^{i\frac{p}{\hbar}x}$ and $e^{-i\frac{p}{\hbar}x}$, which add up to a cosine or sine, as in (2.18), depending on the sign with which we superimpose them. Now through the boundary conditions, we are selecting only a discretized set of these momenta p.

Now we can make use of the powerful statement Eq. (1.71) according to which the solutions of the TISE also dictate the time-evolution for cases with time-independent Hamiltonian (which clearly applies to the one in Eq. (2.11)).

Example 14, Particle in the box dynamics:



left: Consider the particle in state $\Psi(x, t = 0) = \frac{1}{\sqrt{2}}(\phi_1(x) + \phi_2(x)) = \phi_+$. We call this superposition state. As per Eq. (1.71), its time evolution is

$$\Psi(x,t) = c_1(t)\phi_1(x) + c_2(t)\phi_2(x)$$
$$= \frac{1}{\sqrt{2}} e^{-i\frac{E_1}{\hbar}t}\left(\phi_1(x) + \underbrace{e^{-i\frac{(E_2-E_1)}{\hbar}t}}_{\equiv C(t)}\phi_2(x)\right) \tag{2.19}$$

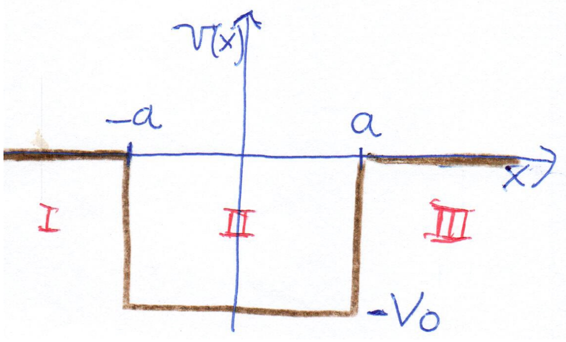
We know that at $t\frac{(E_2-E_1)}{\hbar} = (2n+1)\pi$ for integer n (odd multiples of π), the complex phase factor $C(t) = -1$, while at $t\frac{(E_2-E_1)}{\hbar} = (2n)\pi$ for integer n (even multiples of π) we have $C(t) = 1$.

We thus periodically cycle between a wavefunction ϕ_+ (green in figure) and $\phi_- = \Psi(x, t = 0) = \frac{1}{\sqrt{2}}(\phi_1(x) - \phi_2(x))$ (red in figure), up to the global phase $e^{-i\frac{E_1}{\hbar}t}$, which does not affect the position probability distribution. The corresponding probability densities $|\phi_\pm|^2$ would show a similar structure. This again corroborates the underlying classical picture of the particle bouncing back and forth between the wall. Now please checkout this online app. You should understand the meaning of all its elements now, after reading the documentation.

- When forming the probability density $|\Psi(x,t)|^2$ we see that the global phase $e^{-i\frac{E_1}{\hbar}t}$ drops out, as per our discussion in section 1.6.1. In contrast, the relative phase $C(t)$ between the states $\phi_{1,2}(x)$ turned out crucial, giving us all time dependence.

2.2.2 Finite square well

Instead of the slightly unsettling $V = \infty$ in the preceding section, we now consider the more realistic scenario where the trapping potential for the particle makes a finite jump by an energy V_0 only.



left: To follow Griffith's notation, we adjust the width and zero of energy slightly compared to Eq. (2.10):

$$V(x) = 0 \text{ for } x \leq -a,$$
$$V(x) = -V_0 \text{ for } -a < x \leq a,$$
$$V(x) = 0 \text{ for } x > a, \tag{2.20}$$

where $V_0 > 0$, see figure.

We are for now only looking for energies in the range $-V_0 < E_n < 0$. (You can show that

$\min_x[V(x)] < E$, see Griffith problem 2.2.), and we will look at $E_n > 0$ in section 2.2.3.

As in section 2.2.1, we can treat all three regions separately and then worry about connection conditions. Let us again re-write the TISE as before:

$$\frac{\partial^2}{\partial x^2}\phi_n^{(r)}(x) = -{k_n^{(r)}}^2\phi_n^{(r)}(x), \tag{2.21}$$

for $(r) \in \{I, II, III\}$, where each region has its own wavenumber $k_n^{(r)} = \sqrt{2m[E_n - V(x)]}/\hbar$. We shall use the version where we write the general solution of the TISE in each region in the exponential form, as in section 2.1, with two so far unknown constants per region.

$$\begin{aligned}
\phi_n^{(I)}(x) &= Ae^{ik^{(I)}x} + Be^{-ik^{(I)}x}, \text{ for } x \leq -a \\
\phi_n^{(II)}(x) &= \tilde{C}e^{ik^{(II)}x} + \tilde{D}e^{-ik^{(II)}x} \text{ for } -a < x \leq a, \\
\phi_n^{(III)}(x) &= Fe^{ik^{(III)}x} + Ge^{-ik^{(III)}x} \text{ for } x > a.
\end{aligned} \tag{2.22}$$

Now note that, for the potential (2.20), $k_n^{(I)} = k_n^{(III)} = \sqrt{2mE_n}/\hbar = i\sqrt{-2mE_n}/\hbar \equiv i\kappa_n$, with real $\kappa_n > 0$. Since $E_n < 0$, these two wavenumbers must be imaginary, which we made explicit in the last step. In the second region $k_n^{(II)} = \sqrt{2m(E_n + V_0)}/\hbar \equiv \ell > 0$ is real. Inserting all that, the above Ansatz becomes

$$\begin{aligned}
\phi_n^{(I)}(x) &= Ae^{-\kappa x} + Be^{+\kappa x}, \\
\phi_n^{(II)}(x) &= \tilde{C}e^{i\ell x} + \tilde{D}e^{-i\ell x}, \\
\phi_n^{(III)}(x) &= Fe^{-\kappa x} + Ge^{+\kappa x}.
\end{aligned} \tag{2.23}$$

Now, in order for the wavefunction to be normalizable, we require $A = 0$ and $G = 0$, since the A term would blow up towards $x \to -\infty$ and the G term towards $x \to \infty$. Regarding C and D, note that the potential $V(x)$ is symmetric (even) under $x \leftrightarrow -x$, and you can show that in such cases all wavefunctions must be either even or odd (assignment). We do only the even ones for now, and thus reach

$$\phi_n(x) = \begin{cases} \phi_n^{(I)}(x) & = Be^{+\kappa x}, \text{ for } x \leq -a. \\ \phi_n^{(II)}(x) & = C\cos\ell x \text{ for } -a < x \leq a, \\ \phi_n^{(III)}(x) & = Be^{-\kappa x} \text{ for } x > a, \end{cases} \tag{2.24}$$

with continuity condition at e.g. $x = a$ given by

$$Be^{-\kappa a} = C\cos\ell a, \tag{2.25}$$

$$-\kappa Be^{-\kappa a} = -C\ell\sin\ell a. \tag{2.26}$$

Note the constant C in Eq. (2.24) is different[9] from the previous $\tilde{C}$. Dividing Eq. (2.26) by Eq. (2.25) gives $\kappa = \ell\tan(\ell a)$. This is a transcendental equation[10], which typically is hard to solve. Since κ and ℓ contain the energy E_n, if we can find a solution for some E_n, we have found the eigenenergy.

---

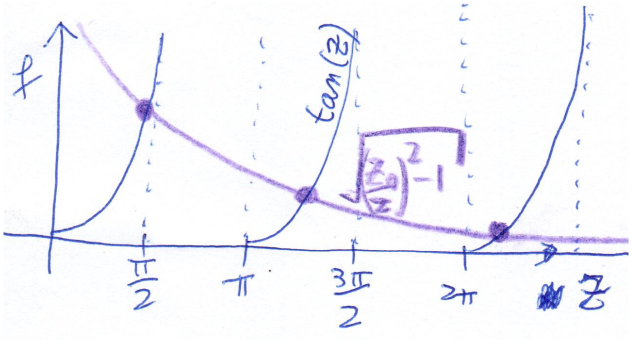
[9] $C/2 = \tilde{C} + \tilde{D}$.

[10] As opposed to a polynomial one

Grifitth discusses a bit how the renaming $z = la$ and $z_0 = a\sqrt{2mV_0}/\hbar$, allows us to recast the equation as

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}, \tag{2.27}$$

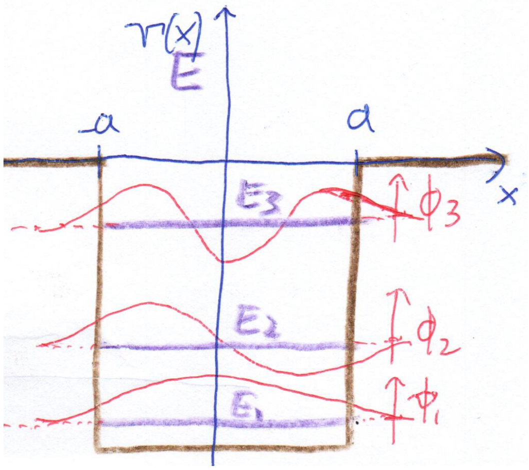
which allows us to understand the solutions graphically:



left: Drawing of $f(z) = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}$ (violet) and different branches of $\tan z$. Values of $z = a\sqrt{2m(E_n + V_0)}/\hbar$ with an intersect, give the allowed energies E_n. *Correction: An important feature missing in the drawing, is that $f(z_0) = 0$, hence the violet line reaches zero, say somewhere at the right edge of the plot.*

Once we know an energy E_n, e.g. Eq. (2.25) will provide B in terms of C, and C can then finally be found from the normalisation. After also sorting out also the odd eigenstates, we finally reach the

Eigenstates and energies of the particle in the finite square well



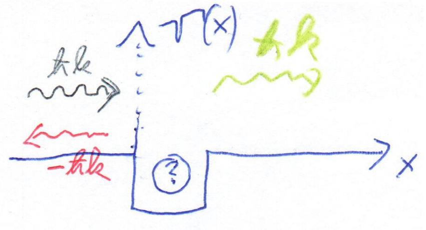
left: Eigenenergies and eigenstates in the finite box, in the same style as for the infinite one earlier.

- We see here one further key feature of quantum mechanics: The wavefunction “leaks” into the region where $E < V(x)$. Classical particles can't do this, since that would imply a negative kinetic energy.
- Another difference to section 2.2.1, that is apparent from the graphical solution of the equation for the eigenenergies, is that there is only a <u>finite number of bound states</u>. Mathematically this is because $f(z)$ becomes imaginary once $z > z_0$, hence there can be no more solutions of Eq. (2.27) (since the LHS of the equation is real).

For this problem, we now expect a new class of behavior for $E > 0$ (= energies higher than the height of the potential wall), which we shall discuss in the next section.

2.2.3 Scattering

For $E > 0$ we can again use (2.22) but this time all $k^{(r)}$ are real, with $k_n^{(I)} = k_n^{(III)} = \sqrt{2mE}/\hbar = k > 0$ and $k_n^{(II)} = \sqrt{2m(E+V_0)}/\hbar = \ell > 0$. For that reason, we cannot remove as many terms from (2.22) due to normalisation as before, but we set $G = 0$ due to the physical picture of scattering that we have in mind:



left: A particle is impinging on the square well with momentum $p = \hbar k$ from the left (black arrow). Due to the potential, it may then be scattered back (red arrow), due to energy conservation with momentum $-p$, or transmitted, keeping momentum p.

The Ansatz for the wavefunction is thus:

$$\begin{aligned}
\phi_n^{(I)}(x) &= Ae^{ikx} + Be^{-ikx}, \text{ for } x \le -a \\
\phi_n^{(II)}(x) &= Ce^{i\ell x} + De^{-i\ell x} \text{ for } -a < x \le a, \\
\phi_n^{(III)}(x) &= Fe^{ikx} \text{ for } x > a. \qquad (2.28)
\end{aligned}$$

We can now set up 4 boundary conditions from (2.28) due to continuity of ϕ and ϕ' at $x = -a$ and $x = a$. This allows us in principle to eliminate 4 of the 5 remaining unknown constants A, B, C, D, F in Eq. (2.22). The last constant cannot be fixed by normalisation, since the Ansatz (2.22) cannot be normalized when all the wavenumbers are real, for the same reasons as discussed in section 2.1. This does not matter here, since we are interested in the question: If a particle is impacting the well from the left, what is its

Transmission probability given by

$$T = |F|^2/|A|^2. \qquad (2.29)$$

- We can understand that using e.g. the concept of probability current in section 1.6.4. Applying Eq. (1.54) to Eq. (2.22) gives a probability current in region I of

$$\begin{aligned}
J^{(I)} &= \frac{\hbar}{m}\mathfrak{Im}\big([A^*e^{-ikx} + B^*e^{ikx}][ikAe^{ikx} + (-ik)Be^{-ikx}]\big) \\
&= \frac{\hbar}{m}\mathfrak{Im}\Big(|A|^2(ik) - |B|^2(ik) + (ik)\underbrace{\left[B^*Ae^{2ikx} - BA^*e^{-2ikx}\right]}_{=2i\mathfrak{Im}[B^*Ae^{2ikx}]}\Big) \\
&= \frac{\hbar}{m}k\big(|A|^2 - |B|^2\big), \qquad (2.30)
\end{aligned}$$

providing the interpretation of $|A|^2$ as the incoming current density and $|B|^2$ as reflected current density. Note $\hbar k/m = v$ is the velocity. Obtaining $|F|^2$ as transmitted current density is much easier.

Let us once explicitly go through the solution of the piecewise TISE for this problem, we will then only state the results for a few other applications later. Then you shall also practice it in an assignment for one of those problems. The 4 continuity conditions are:

$$Ae^{-ika} + Be^{ika} = Ce^{-i\ell a} + De^{i\ell a} \qquad \text{from continuity of } \phi_n \text{ at } x = -a, \tag{2.31}$$

$$Ce^{i\ell a} + De^{-i\ell a} = Fe^{ika} \qquad \text{from continuity of } \phi_n \text{ at } x = a, \tag{2.32}$$

$$(ik)Ae^{-ika} - (ik)Be^{ika} = (i\ell)Ce^{-i\ell a} - (i\ell)De^{i\ell a} \qquad \text{from continuity of } \phi_n' \text{ at } x = -a, \tag{2.33}$$

$$(i\ell)Ce^{i\ell a} - (i\ell)De^{-i\ell a} = (ik)Fe^{ika} \qquad \text{from continuity of } \phi_n' \text{ at } x = a, \tag{2.34}$$

We now first find C and D in terms of F, using Eq. (2.32)±Eq. (2.34)/(il) to reach

$$C = \frac{1}{2}Fe^{ia(k-\ell)}(1 + \frac{k}{\ell}), \tag{2.35}$$

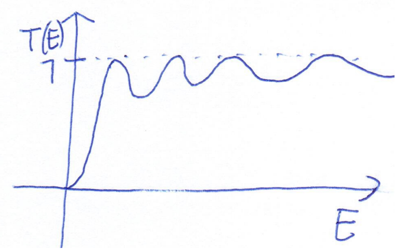
$$D = \frac{1}{2}Fe^{ia(k+\ell)}(1 - \frac{k}{\ell}), \tag{2.36}$$

We can now eliminate C and D, while taking Eq. (2.31)+ Eq. (2.33)/(ik) to reach

$$2Ae^{-2ika} = F\left[\cos(2la) - i(k/\ell + \ell/k)\sin(2la)\right]. \tag{2.37}$$

Alternatively, you can run these 4 equations for 5 unknowns into `mathematica` and hit `Solve[]`. Inserting the last line into (2.29), and expressing k and ℓ in terms of the relevant energies and potentials gives us the

Transmission probability through a finite square well



left: As shown on the left:

$$T = \frac{1}{1 + \frac{V_0^2}{4E(E+V_0)}\sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right)} \tag{2.38}$$

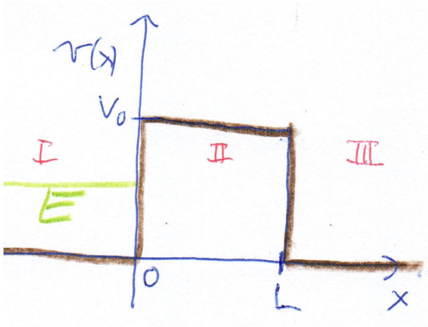
- A first thing we notice is that $T \approx 0$ for small E. This is surprising, since $E > 0$ means the particle has more energy than the potential energy at all x and thus classically would pass with 100%. This is a manifestation of quantum reflection. The same would be true for a single potential step (where $V(x) = -V_0$ also at all $x > a$.
- From (2.38), $T = 1$ whenever $\frac{2a}{\hbar}\sqrt{2m(E+V_0)} = n\pi$ for $n \in \mathbb{Z}$ implying perfect transmission. We can reform this to give

$$E_n + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}, \tag{2.39}$$

which are exactly the energies above zero where we would expect an eigenstate of the infinite box. We see that resonances with bound-states (or metastable states) significantly affect the scattering behaviour. This feature is crucial for experimental interrogation, particularly in nuclear and particle physics. See also the section on Griffith, on the S-matrix (2.7).

- In this section, all values of $E > 0$ gave a solution of the TISE. Together with section 2.2.2 the finite well thus has a combination of a discrete spectrum $E_n < 0$ and a continuous spectrum, for $E > 0$. There are many other examples of this.
- The wavefunctions for $E > 0$ that reach all the way to $x \to \pm\infty$ are called scattering states.

2.2.4 Square barrier



left: We can invert the potential (2.20), by letting $V(x) > V_0 > 0$ within some range (now $x = 0$ to $x = L$).

We then consider the same scattering Ansatz as proposed in section 2.2.3, which can be solved with the same techniques. Here we are mainly interested in the case $0 < E < V_0$. As you have learned in PHY106, this gives rise to

Quantum tunneling with transmission probability (2.29), in the limit $E \ll V_0$ and $\kappa L \gg 1$ given by

$$T = e^{-2\kappa L}, \text{ for } \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}. \tag{2.40}$$

- You can find this formula by applying the techniques of section 2.2.3 to this modified setting (exercise).
- Transmission through the barrier for $E < V_0$ is classically impossible, but allowed in quantum tunnelling.
- We had discussed the important points of (2.40) and physics examples where tunnelling is crucial quite extensively in PHY106, week9, hence we don't repeat that here.

Week ④

PHY 303 Quantum Mechanics
Instructor: Sebastian Wüster, IISER Bhopal, 2023

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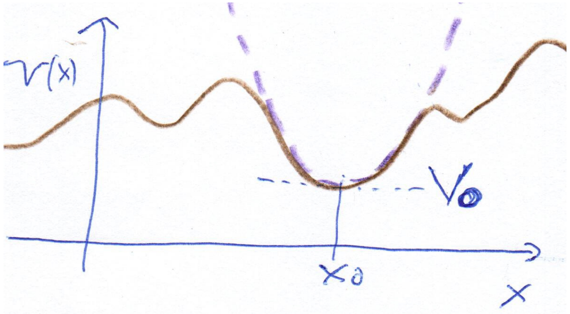
2.3 Quantum harmonic oscillator

We now finally go beyond piecewise constant potentials, to look at the harmonic oscillator potential

$$V(x) = \frac{1}{2} m\omega^2 x^2. \tag{2.41}$$

This is very important, simply because near a local minimum, any potential will look like a harmonic oscillator potential:



left: Near a local minimum at x_0, we can write $V(x) = \underbrace{V(x_0)}_{=V_0} + \frac{1}{2} V''(x)\Big|_{x=x_0} (x-x_0)^2 + \mathcal{O}(x-x_0)^3$. Defining $V''(x)\Big|_{x=x_0} = m\omega^2$, this gives us (2.41).

Because of the broad importance of the quantum harmonic oscillator, we even provide two different methods to solve its TISE

$$\left[\frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2\right] \phi_n(x) = \underbrace{\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega^2 x^2\right]}_{=\hat{H}} \phi_n(x) = E_n \phi_n(x), \tag{2.42}$$

an algebraic method and the more direct solution via a power series.

2.3.1 Algebraic method

Let us define new linear combinations out of the position and momentum operators, so-called

Ladder operators

$$\hat{a}_{\pm} = \frac{1}{\sqrt{2m\hbar\omega}} (\mp i\hat{p} + m\omega\hat{x}) = \frac{1}{\sqrt{2m\hbar\omega}} \left(\mp\hbar\frac{\partial}{\partial x} + m\omega\hat{x}\right). \tag{2.43}$$

where the + one is called raising operator and the one with − lowering operator.

It turns out that with these operators, we can re-write the TISE Eq. (2.42) as

$$\hbar\omega\left[\hat{a}_+\hat{a}_- + \frac{1}{2}\right]\phi_n(x) = E_n\phi_n(x). \tag{2.44}$$

- Griffith discusses some motivation why we choose the linear combinations (2.43), essentially trying to bring the form $u^2 + v^2$ in the Hamiltonian into a product $(u - iv)(u + iv)$.
- However now we have to be careful since the Hamiltonian contains operators, where the ordering may be important. For example $x\frac{\partial}{\partial x}f(x) \neq \frac{\partial}{\partial x}[xf(x)]$.
- See the detailed derivation from (2.42) to (2.44) in Griffith.

In that derivation, we can use the

Commutator of ladder operators:

$$\left[\hat{a}_-, \hat{a}_+\right] \equiv \hat{a}_-\hat{a}_+ - \hat{a}_+\hat{a}_- = 1. \tag{2.45}$$

- You may remember from matrix multiplication, that usually we do not have $\underline{\underline{A}} \cdot \underline{\underline{B}} = \underline{\underline{B}} \cdot \underline{\underline{A}}$. Since operators can be viewed as infinite dimensional matrices (section 10), you should find Eq. (2.45) at least plausible.
- Proof: We must show identities involving operators by applying operators onto a testfunction $f(x)$, since e.g. having a dangling derivative as in $x\frac{\partial}{\partial x}$ that is not applied onto anything does not make sense. In this way, let us find an easier commutator first, namely

  $$\left[\hat{x}, \hat{p}\right] = (i\hbar). \tag{2.46}$$

  To see this, we write

  $$\begin{aligned}\left[\hat{x}, \hat{p}\right]f(x) &= \left(x(-i\hbar\frac{\partial}{\partial x}) - (-i\hbar\frac{\partial}{\partial x})x\right)f(x) \\ &= (-i\hbar)\left(xf'(x) - [xf(x)]'\right) = (-i\hbar)\left(xf'(x) - [1f(x) + xf'(x)]\right) = (i\hbar)f(x).\end{aligned} \tag{2.47}$$

  Since this is true for <u>any</u> testfunction $f(x)$, we have shown the operator identity (2.46).

  Using either Eq. (2.46) and the definition Eq. (2.43), or the same technique as above directly from Eq. (2.43), you can show (2.45) as an exercise.
- We will learn many additional useful rules regarding commutators in chapter 3 and discuss them much more.

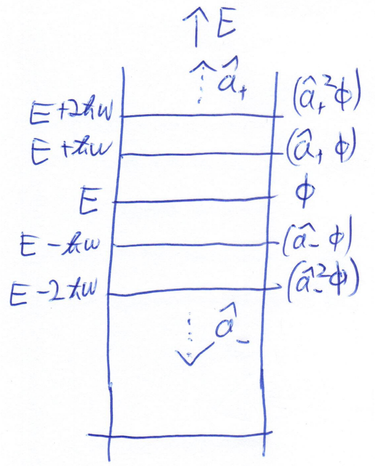
In (2.44) we just rewrote the TISE with some weird operators. Armed with the commutator (2.45), we can now attack the crucial argument why this is useful. Namely we can show that if $\phi(x)$ solves the TISE for energy E, then $\hat{a}_+\phi(x)$ solves it for energy $E+\hbar\omega$. Proof: As a first step, we see that using (2.45), we can write Eq. (2.44) also as

$$\hbar\omega\left[\hat{a}_-\hat{a}_+ - \frac{1}{2}\right]\phi_n(x) = E_n\phi_n(x). \tag{2.48}$$

Then

$$\hbar\omega\left[\hat{a}_+\hat{a}_- + \frac{1}{2}\right](\hat{a}_+(\phi_n(x))) = \hbar\omega\big[\hat{a}_+ \underbrace{(\hat{a}_-\hat{a}_+)\phi_n(x)}_{Eq.\ \overset{(2.48)}{=}(E_n/(\hbar\omega)+\frac{1}{2})\phi_n} + \frac{1}{2}(\hat{a}_+(\phi_n(x))\big] = \big(E_n+\hbar\omega\big)(\hat{a}_+(\phi_n(x)). \tag{2.49}$$

which means that $\hat{a}_+(\phi_n(x))$ solves the TISE with energy $E+\hbar\omega$ as claimed. Similarly we can show that $\hat{a}_-(\phi(x))$ solves it for energy $E-\hbar\omega$.



left: This now explains why we call $\hat{a}_\pm$ ladder operators. Given ANY solution of the problem $\phi(x)$ we are raising the energy with $\hat{a}_+$, lowering it with $\hat{a}_-$, and thus can build a ladder of different energy values, see diagram on the left.

Of course to use this, we first need at least one solution $\phi(x)$, which we don't have yet. To get one, consider repeated application of $\hat{a}_-$. Since the energy is reduced everytime, at some point it would have to become negative. However it is not possible that $E < \min_x V(x)$ (see e.g. Griffith Problem 2.2). This means that at some point we require $\hat{a}_-\phi_0(x) = 0$ for some "lowest step" on the ladder ϕ_0, to terminate generating lower and lower energy solutions[11]. Writing this explicitly from (2.43) in terms of the position and momentum operator:

$$\frac{1}{\sqrt{2m\hbar\omega}}\left(-i\hbar\frac{\partial}{\partial x} - im\omega\hat{x}\right)\phi_0 = 0. \tag{2.50}$$

This differential equation is now easy to solve, in contrast to the original one. We sort things a bit and then integrate both side':

$$\frac{d\phi_0}{dx} = -\frac{m\omega}{\hbar}x\phi_0 \Rightarrow \int\frac{d\phi_0}{\phi_0} = -\frac{m\omega}{\hbar}\int dx\, x \Rightarrow \ln\phi_0 = -\frac{m\omega}{2\hbar}x^2 + \text{const} \rightarrow \phi_0(x) = \mathcal{N}e^{-\frac{x^2}{2\sigma^2}}. \tag{2.51}$$

with $\sigma = \sqrt{\hbar/m/\omega}$. Since we had demanded $\hat{a}_-\phi_0(x) = 0$, we can directly see from Eq. (2.44) that the energy of this state is $E_0 = \hbar\omega/2$. With that we have now solved the TISE for the

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[11] See Griffith for one other possibility, and why that does not happen.

Quantum harmonic oscillator For $n = 0, 1, 2, 3\cdots$ the solutions are

$$\phi_n(x) = \mathcal{N}_n(\hat{a}_+)^n\phi_0(x) = \mathcal{N}_n(\hat{a}_+)^n e^{-\frac{1}{2}\frac{x^2}{\sigma^2}}/(\pi\sigma^2)^{1/4}, \tag{2.52}$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{2.53}$$

with eigenfunction ϕ_n, normalisation factor $\mathcal{N}_n$, zero point uncertainty $\sigma = \sqrt{\hbar/(m\omega)}$.

- To generate all other solutions from Eq. (2.51) we used our earlier result (2.49). For example we can generate $\phi_1(x) \sim (\hat{a}_+)^1 e^{-\frac{1}{2}\frac{x^2}{\sigma^2}}$ and then normalize it. Using Eq. (2.43), this gives us

$$\begin{aligned}\phi_1(x) &= \mathcal{N}_1\frac{1}{\sqrt{2m\hbar\omega}}\left(-i\hbar\frac{\partial}{\partial x} + im\omega\hat{x}\right)e^{-\frac{m\omega}{2\hbar}x^2}\\ &= \frac{\mathcal{N}_1}{\sqrt{2m\hbar\omega}}\left(-i\hbar(-\frac{m\omega}{\hbar}x) + im\omega x\right)e^{-\frac{m\omega}{2\hbar}x^2}\\ &= i\mathcal{N}_1\omega\sqrt{\frac{2}{\hbar\omega}}\left(\frac{x}{\sigma}\right)e^{-\frac{1}{2}\frac{x^2}{\sigma^2}}. \end{aligned} \tag{2.54}$$

  We will provide drawings of this function later.

- The unknown integration constant *const* turned into $\mathcal{N}$ in (2.51) and $\mathcal{N}_n$ in (2.52) and has to be fixed for each separately by normalisation using Eq. (1.6.1).

So far we had only seen that $\hat{a}_+\phi_n(x) \sim \phi_{n+1}(x)$ without knowing the proportionality constant. We can derive the constant following steps in Griffith, 3rd edition, and then know the complete

Action of ladder operators on harmonic oscillator states:

$$\hat{a}_+\phi_n(x) = \sqrt{n+1}\phi_{n+1}(x), \qquad \hat{a}_-\phi_n(x) = \sqrt{n}\phi_{n-1}(x). \tag{2.55}$$

- During that proof, you will also show that $\hat{a}_-^\dagger = \hat{a}_+$, i.e. the two operators are the Hermitian adjoints of each other, see Eq. (1.24).
- For that reason, you will mostly find the simpler notation: $\hat{a}_- \rightarrow \hat{a}$, $\hat{a}_+ \rightarrow \hat{a}^\dagger$.
- Using Eq. (2.55), you can show that $\mathcal{N}_n = 1/\sqrt{n!}$ in Eq. (2.52).

We will discuss the physics of the quantum SHO and detailed shape of wavefunctions shortly, first we shall see one more completely different method to arrive at the above solutions.

2.3.2 Analytical method

The solution of the preceding section is very elegant, but very tricky. I would not have thought of it myself, for sure, would you?. We can also try to solve the TISE (2.42) in a more generally applicable way. Let us first move to dimensionless units for space $\xi = x/\sigma$ and energy $K_n = 2E_n/(\hbar\omega)$. Drawing on section 2.3.1, this means that we measure space in units of the zero point uncertainty and energy in units of $\hbar\omega$. Converting the differential operator in (2.42), we see that this tidies the equation up quite a bit, and we reach

$$\frac{d^2}{d\xi^2}\phi_n(\xi) = (\xi^2 - K_n)\phi_n(\xi). \tag{2.56}$$

We first see what happens when $|\xi| \to \infty$ and hence $\xi^2 \gg K$, in that case we have $\frac{d^2}{d\xi^2}\phi_n(\xi) = \xi^2\phi_n(\xi)$. This has the <u>approximate</u> solution

$$\phi_n(\xi) \approx Ae^{-\xi^2/2} + Be^{\xi^2/2}. \tag{2.57}$$

To see this take the double derivative of (2.57) wrt. ξ, and in the resultant expression use that $|\xi| \to \infty$ which means only the highest powers of ξ in any term need to be considered. Only the term $\sim A$ can be normalized, so we must chose $B = 0$. Now that we know how the function has to behave at large ξ, let us build this form into our solution attempt, by defining

$$\phi_n(\xi) \approx h(\xi)e^{-\frac{\xi^2}{2}}. \tag{2.58}$$

(Technically we should write $h_n(\xi)$, but we shall suppress that until Eq. (2.65)). We can plug (2.58) into the TISE (2.56) (see Griffith) and reach an equation for $h(\xi)$

$$\frac{d^2h(\xi)}{d\xi^2} - 2\xi\frac{dh(\xi)}{d\xi} + (K-1)h(\xi) = 0. \tag{2.59}$$

To solve this, we express the solution in terms of a

Power series expansion:

$$h(\xi) = \sum_{j=0}^{\infty} a_j\xi^j. \tag{2.60}$$

We then insert (2.60) into (2.59), which gives

$$\sum_{j=0}^{\infty} \underbrace{[(j+1)(j+2)a_{j+2} - 2ja_j + (K-1)a_j]}_{=0}\xi^j = 0. \tag{2.61}$$

Since all the different powers of ξ are linearly independent, the coefficient of all ξ^j have to vanish separately, which gives us:

$$a_{j+2} = \frac{2j+1-K}{(j+1)(j+2)}a_j. \tag{2.62}$$

This is a recursion formula, such that if we know a_0 and a_1, it gives us all the higher a_j. One can show, that the series (2.60) with coefficients fulfilling (2.62) must terminate, i.e. possess a highest $j = n$ such that all $a_{j'} = 0$ for $j' > n$ (see e.g. Griffith). Essentially, if it did not, the resultant function would not be normalizable.

Note that Eqs. (2.60) and (2.62) effectively set up two independent power series for the even and odd part of the function

$$h_{\text{even}}(\xi) = a_0 + a_2\xi^2 + a_4\xi^4 + \cdots \qquad \text{(even)}, \tag{2.63}$$

$$h_{\text{odd}}(\xi) = a_1\xi + a_3\xi^3 + a_5\xi^5 + \cdots \qquad \text{(odd)} \tag{2.64}$$

We can see that the only way to terminate the series at $j = n$ is if $2n + 1 = K$. Since it only terminates one of the even or odd series, the other one must have been fully zero due to $a_0 = 0$ or $a_1 = 0$. Alternatively one can also show that an even potential $V(x) = V(-x)$ gives rise to either even or odd eigenfunctions (exercise/assignment). We can rewrite $2n+1 = K$ into $E_n = (n+1/2)\hbar\omega$, so we just re-discovered Eq. (2.53). From the discussion so far we see that $h(\xi)$ which terminates at $j = n$ is a polynamical of degree n. All up we find the

Explicit eigenfunctions of the quantum harmonic oscillator as

$$\phi_n(x) = \mathcal{N}_n H_n\left(\frac{x}{\sigma}\right) e^{-\frac{1}{2}\frac{x^2}{\sigma^2}}, \tag{2.65}$$

with $\mathcal{N}_n = (\pi\sigma^2)^{-1/4}(2^n n!)^{-1/2}$ and $H_n(\xi)$ a Hermite polynomial of degree n.

- The lowest Hermite polynomials are

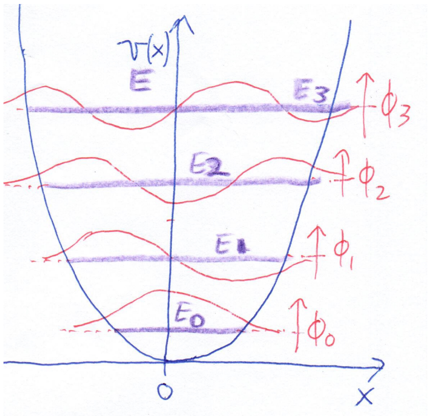
$$H_0 = 1, \tag{2.66}$$

$$H_1 = 2x, \tag{2.67}$$

$$H_2 = 4x^2 - 2, \tag{2.68}$$

$$H_3 = 8x^3 - 12x. \tag{2.69}$$

  Note, that with the expression for H_1, (2.65) of course agrees with the first excited state we had found in Eq. (2.54).



left: On the left we draw $V(x)$, E_n and $\phi_n(x)$ for the harmonic oscillator in the same style as for particle in the box (PIB) before (near Eq. (2.18)).

- As for the PIB, they alternate between even and odd.
- As for the finite-PIB, wavefunctions extend exponentially decaying into the classically forbidden region where $V(x) > E$.
- Unlike the PIB, the quantized energies are equidistant $E_{n+1} - E_n = \hbar\omega$.

- Again, the lowest energy is nonzero. $E = \hbar\omega/2$ is called the zero-point energy. You can calculate also the position uncertainty in the ground-state (see assignment 2, Eq. (1.35)) and you shall find $\sigma_x = \sigma/\sqrt{2}$ (hence the choice of variable letter). This is due to what is called zero-point motion.

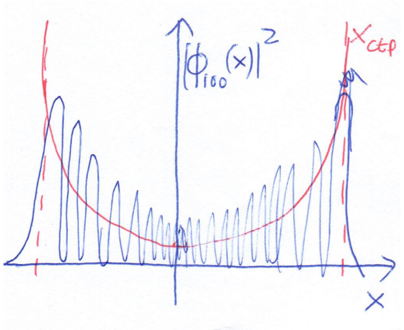
The procedure that we have used to solve the differential equation (2.56) is more generally useful:

(i) First find asymptotic solutions at large $|\xi| \to \infty$.

(ii) Build the structure of that solution into an Ansatz such as (2.58), and then solve for the detailed form with a power series such as (2.60).

On first sight, the solutions $\phi_n(x)$ seem to have little to do with what we know of the classical harmonic oscillator. However the connections are only slightly hidden. Consider the time-averaged probability distribution of the classical oscillator. We know it follows $x(t) = x_{\text{ctp}} \sin(\omega t)$. If you look at a large random ensemble of oscillators, the probability $\rho(x)$ to find in between position x and $x + dx$ must be $\rho(x) \sim dx/v(x)$. Since $v(t) = \omega x_{\text{ctp}} \cos(\omega t)$ we can write[12] $\rho(x) \sim (\omega\sqrt{x_{\text{ctp}}^2 - x^2})^{-1}$. But this stil has the wrong units and is nor normalised. After normalising this to one, it becomes $\rho(x) = (\pi\sqrt{x_{\text{ctp}}^2 - x^2})^{-1}$. We can now see the

Example 15, Correspondence principle:



left: The sketch on the left shows a very high SHO state $\phi_n(x)$ (blue), and the classical probability distribution $\rho(x)$ (red). We see that the average amplitude of the quantum state precisely follows $\rho(x)$. If we now were e.g. averaging over a few adjacent SHO states, we recover the classical result.

There are more signs of the underlying classical physics: In example 13, we had seen how the PIB states can be decomposed in plane waves that correspond to a classical particle bouncing back and forth. In that case, the probability distribution $\rho(x) \sim \sin^2(p/\hbar x)$, which means the distance between zeros gave some indication of the momentum (velocity). You see in example 15 how the distance between zeros decreases in the centre and increases at the flanks. This again, reflects that we know the oscillator will move fastest around $x = 0$ and slowest near $x = x_{\text{ctp}}$ (the classical turning point).

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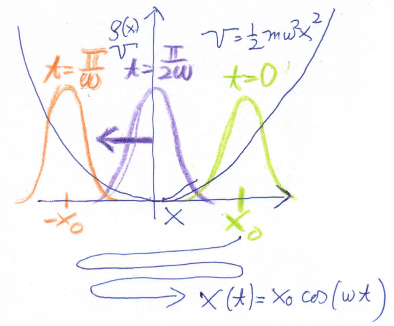
[12] Using $\cos^2 + \sin^2 = 1$.

Example 16, Making the quantum oscillator classical again: Some more hidden known physics:



left: If we e.g. solve the TDSE 1.2 on a computer, starting from a Gaussian wavefunction that is offset by x_0 from the centre: $\Psi(x,t=0)=\phi_0(x-x_0)$, the probability density preserves a Gaussian shape $\rho(x)\sim e^{-(x-x_0(t))^2/\sigma^2}$, with $x_0(t)=x_0\cos(\omega t)$. Besides retaining the zero-point uncertainty σ (independent of time), the centre of the position space distribution thus just does the classical oscillation.

You can again check this out life using this online app. *Analytical proof and discussion: Assignment 4.*

Example 17, Quantum harmonic oscillators in science: Since every potential looks like a harmonic oscillator near local minima (and hence near stable equilibrium points), as discussed at the beginning of section 2.3, the importance of the QSHO cannot be overstated. You will encounter it again for:

- Vibrations of molecules around their equilibrium bond lengths.
- Lattice vibrations of ions in solid materials, e.g. metals.
- Ions and atoms trapped in electromagnetic fields (and otherwise vacuum), for e.g. quantum computing.

You will also see, that operators such as $\hat{a}_{\pm}$ and the mathematical rules induced by (2.45) can also be used to climb a ladder in terms of "particle number", instead of oscillator energy. Some of the concepts in this section thus form the basis of many-body quantum physics, quantum field theory and particle physics.

Week ⑤

PHY 303 Quantum Mechanics
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2.4 Free particles

We now return to the free particle that we had started in section 2.1 and then postponed after some initial considerations. Using the plane-wave eigenstates (2.4), we want to now assemble time-dependent solutions and physically meaningful wavefunctions (that are normalized).

2.4.1 Travelling waves

Earlier we had solved the free TISE (2.2) using the solution:

$$\phi(x) = Ae^{ikx} + Be^{-ikx}, \tag{2.70}$$

with $k = \sqrt{2mE}/\hbar$. These are stationary states with energy E, hence according to (1.64) we know their time-evolution

$$\phi(x,t) = (Ae^{ikx} + Be^{-ikx})e^{-i\frac{E}{\hbar}t} = Ae^{ik\left(x-\frac{\hbar k}{2m}t\right)} + Be^{-ik\left(x+\frac{\hbar k}{2m}t\right)},. \tag{2.71}$$

where we have used $E = \hbar^2k^2/(2m)$. Comparing this with e.g. PHY106 Week 3, we recognize these as a left-moving plus a right-moving plane wave with <u>phase velocity</u> $v = \hbar k/(2m) = \sqrt{E/(2m)}$.

Unfortunately, from classical physics we rather expect a phase velocity $v = \hbar k/(m) = \sqrt{2E/m}$. However, we had already seen in PHY106, that it does not really make sense to attempt to define a velocity from Eq. (2.71). This wave represents a particle that already IS everywhere in space, and a definition of velocity requires the time it takes to get from some point x_0 to some other point x_1. Thus we have to localize our particle, which will simultaneously sort out the problem with normalisation discussed in section 2.1.

2.4.2 Wavepackets

We had also already seen in PHY106 Week 5 how you can localize a wave by superimposing a few waves with different wavelengths, such that they constructively interfere near say $x \approx 0$, but cancel each other at larger $|x|$. This is used in the

Free particle wavepacket with time-dependent wavefunction

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \tilde{\phi}(k) e^{i(kx - \frac{\hbar k^2}{2m} t)} \tag{2.72}$$

- While somewhat hidden, (2.72) is just the same statement as (1.71), applied to the free particle. The translation is as follows: Since we saw in (2.1), that the free particle Hamiltonian has a continuous spectrum, we have to convert the sum $\sum_n$ into an integration $\int dk$, renaming the discrete index n into a continuous index/variable k. The coefficient $c_n(0)$ is called $\phi(k)/\sqrt{2\pi}$ now. The basis functions $\phi_n(x)$ now are $\phi(x,p)$ from (2.4).
- Let us check out the normalisation of $\Psi(x,t)$. We can write

$$\begin{aligned}
\int_{-\infty}^{\infty} dx |\Psi(x,t)|^2 &\overset{Eq.\ (2.72)}{=} \frac{1}{(2\pi)} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dk' \left[\tilde{\phi}^*(k) e^{-i(kx - \frac{\hbar k^2}{2m} t)}\right] \left[\tilde{\phi}(k') e^{i(k'x - \frac{\hbar k'^2}{2m} t)}\right] \\
&= \frac{1}{(2\pi)} \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} dk' \underbrace{\left[\int_{-\infty}^{\infty} dx\, e^{i(k'-k)x}\right]}_{\overset{Eq.\ (2.8)}{=}(2\pi)\delta(k-k')} \left[\tilde{\phi}^*(k) e^{+i\frac{\hbar k^2}{2m} t}\right] \left[\tilde{\phi}(k') e^{-i\frac{\hbar k'^2}{2m} t}\right] \\
&= \int_{-\infty}^{\infty} dk |\tilde{\phi}(k)|^2.
\end{aligned} \tag{2.73}$$

  In steps like the first line, it is very important to rename the second "dummy index" from k to k', otherwise you would get into a total mess. What we have shown, is that $|\Psi(x,t)|^2$ is normalized to one in position space (at all times), if $\tilde{\phi}(k)$ is normalized in "k-space", which we will assume to be the case, in the following.
- We now succeeded in creating a normalized wavepacket that is a solution of the TDSE (1.2). Usually we want to solve the TDSE as an initial value problem as discussed in section 1.4. Suppose we know $\Psi(x,0)$, how do we pick $\tilde{\phi}(k)$ in (2.72) so that it gives the correct initial state? We can use the

Fourier transform: We can decompose any function as

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \tilde{f}(k) e^{ikx} \tag{2.74}$$

in terms of complex plane waves e^{ikx}. The coefficients $\tilde{f}(k)$ of the decomposition can be found from the Fourier transform

$$\tilde{f}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, f(x) e^{-ikx} \tag{2.75}$$

The statement (2.74) is then called inverse Fourier transform.

- The two expressions Eqs. (2.74) and (2.75) together are also called Plancherel's theorem.

- We can understand it based on section 1.5.4. The plane waves e^{ikx} form a basis of the function space. (2.74) is thus nothing else than (1.18) (with a continuous index). When we find the coefficients as in (2.75), this is exactly the scalarproduct (b_n, f) given below (1.18).

- The Fourier transform generalises the Fourier series (1.20) from periodic to not necessarily periodic functions.

- $\tilde{f}(k)$ is called the Fourier space representation of the function $f(x)$. k is called the Fourier space.

- The Fourier transform clearly is among the most useful techniques/theorems in science and engineering. It is used in virtually all of its fields. You use it for data analysis, signal processing, mathematical methods. As we shall see, it is particularly central to quantum mechanics.

- We can now easily apply Eq. (2.75) to find the Fourier spectrum of any initial wavefunction.

  $$\tilde{\phi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, e^{-ikx} \Psi(x, 0), \tag{2.76}$$

  i.e. we project the initial state onto the plane wave e^{-ikx} using a scalar product to find $\tilde{\phi}(k)$.

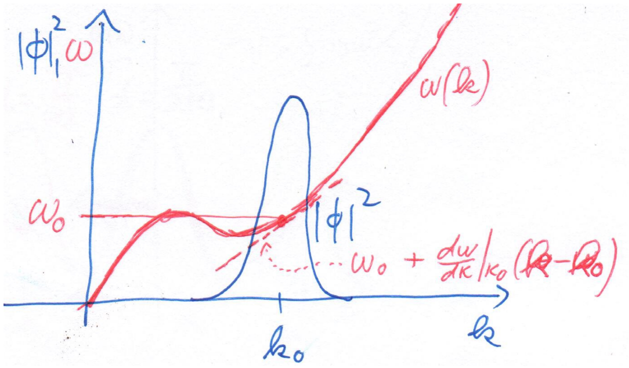
- We had written down everything here in terms of a position x and wavenumber k, however the result is purely mathematical. We can use any other pair of variables (e.g. time t and frequency ω), which are then called a Fourier transform pair.

2.5 Group velocity

Let us now see how the wavepacket (2.72) has also resolved our earlier confusion in section 2.4.1 about the phase-velocity of the free particle not quite matching with what one would expect. The following discussion is not really special to quantum physics, but to any wave physics, hence let us rename the frequencies in the wavepacket into the usual notation

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \tilde{\phi}(k) e^{i(kx - \omega(k)t)}. \tag{2.77}$$

In (2.72) we had the special case of a dispersion relation $\omega(k) = E/\hbar = \hbar k^2/(2m)$.



left: For a general unknown dispersion relation $\omega(k)$, let us assume the Fourier spectrum $\tilde{\phi}(k)$ of the wave function is relatively narrow in Fourier space near some k_0, as shown in the drawing on the left. It then makes sense, over the range of k where $|\tilde{\phi}(k)| > 0$, to approximate $\omega(k) \approx \omega(k_0) + \underbrace{\frac{d\omega(k)}{dk}}_{\equiv\omega'}(k-k_0) + \mathcal{O}[(k-k_0)^2]$ using the Taylor series (1.19).

We insert this into Eq. (2.77) and change integration variable from k to $\bar{k} = k - k_0$ and then have

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\bar{k}\, \tilde{\phi}(k_0 + \bar{k}) e^{i\{(k_0+\bar{k})x - [\omega(k_0)+\omega'\bar{k}]t\}}$$
$$= \frac{1}{\sqrt{2\pi}} e^{i[-\omega(k_0)+k_0\omega']t} \int_{-\infty}^{\infty} d\bar{k}\, \tilde{\phi}(k_0 + \bar{k}) e^{i[(k_0+\bar{k})(x-\omega' t)])}. \tag{2.78}$$

If we use the last expression to compare $\Psi(x,0)$ with $\Psi(x,t)$ we see that the part inside the integral is just changed by $x \to x - \omega' t$. The part outside the integral is just a complex phase factor, so it will drop out when calculating the probability density $|\Psi(x,t)|^2$ We conclude that this wavepacket moves with the

Group velocity

$$v_g = \left.\frac{d\omega(k)}{dk}\right|_{k=k_0}. \tag{2.79}$$

- This expression pertains to any wavepacket, not just the matter wave free particle. For example for electro-magnetic waves (photons) in vacuum, we have $\omega = kc$, where c is the speed of light, hence $v_g = c$. The dispersion relation typically changes in a medium though.
- For the matter wave packet (2.72) $\omega(k) = \hbar k^2/(2m)$ hence $v_g = \hbar k_0/m$, which is now finally the velocity we expect (namely $= p_0/m$. We conclude that the physical velocity of a particle is the group velocity of its wavepacket.

2.6 The Gaussian wavepacket

We had already seen in PHY106 that the

Gaussian quantum wavepacket

$$\Psi(x,0) = \frac{1}{(\pi\sigma^2)^{\frac{1}{4}}} e^{-\frac{(x-x_0)^2}{2\sigma^2}} \exp\left[ik_0(x-x_0)\right] \tag{2.80}$$

with $k_0 = \frac{p_0}{\hbar}$ can provide a reasonably nice localisation of the particle in a range σ near x_0, and a reasonably well defined momentum in a range $\sim 1/\sigma$ near $p_0 = \hbar k_0$.

- Specifically (see assignments 1 and 2), we find $\langle\hat{x}\rangle = x_0$, $\langle\hat{p}\rangle = p_0$, $\sigma_x = \sigma/\sqrt{2}$ and $\sigma_p = \hbar/(\sqrt{2}\sigma)$
- The Gaussian wavepacket is thus a minimum uncertainty wavepacket, since it minimizes the RHS of Heisenberg's uncertainty principle Eq. (1.47), see assignment 2.
- This means a wavepacket such as (2.80) is "as close as one can get" to the idea of a classical phase-space coordinate (x, p).

Classically, the evolution of a free particle at position x_0 with momentum p_0 is simply motion with uniform velocity $x(t) = x_0 + (p_0/m)t$. What will change quantum mechanically?

For that, we see that (2.80) is a special case of (2.72), if we can find the correct Fourier-space wavefunction $\phi(k)$. For this we use the inverse Fourier transform as in Eq. (2.76). We find that the Fourier transform of a Gaussian is a Gaussian. Below is a proof. If you have seen complex analysis and the residue theorem, read the proof below. If not, don't worry about the residue theorem, but you will have to believe me the first and last line. Using the short-hand $\mathcal{N} = (\pi\sigma^2)^{-\frac{1}{4}}$,

$$\begin{aligned}
\tilde{\phi}(k) &= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dx\, e^{-ikx}\Psi(x,0) = \frac{\mathcal{N}}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dx\, e^{-ikx}e^{-\frac{[x-x_0]^2}{2\sigma^2}}\exp\left[ik_0(x-x_0)\right] \\
&= \frac{\mathcal{N}}{\sqrt{2\pi}}e^{-ix_0k}e^{-\frac{\sigma^2}{2}(k_0-k)^2}\int_{-\infty}^{\infty} dx\, e^{-\frac{\left[x-x_0-i\sigma^2(k_0-k)\right]^2}{2\sigma^2}} \\
&\overset{z=x-x_0-i\sigma^2(k_0-k)}{=} \frac{\mathcal{N}}{\sqrt{2\pi}}e^{-ix_0k}e^{-\frac{(k_0-k)^2}{2\sigma_k^2}}\int_{-\infty-i\sigma^2(k_0-k)}^{\infty-i\sigma^2(k_0-k)} dz\, e^{-\frac{z^2}{2\sigma^2}} \\
&\overset{\text{residue theorem}}{=} \frac{\mathcal{N}}{\sqrt{2\pi}}e^{-ix_0k}e^{-\frac{(k_0-k)^2}{2\sigma_k^2}}\underbrace{\int_{-\infty}^{\infty} dz\, e^{-\frac{z^2}{2\sigma^2}}}_{=\sqrt{2\pi}\sigma} \\
&= \frac{1}{(\pi\sigma_k^2)^{1/4}}e^{-ix_0k}e^{-\frac{(k_0-k)^2}{2\sigma_k^2}},
\end{aligned} \tag{2.81}$$

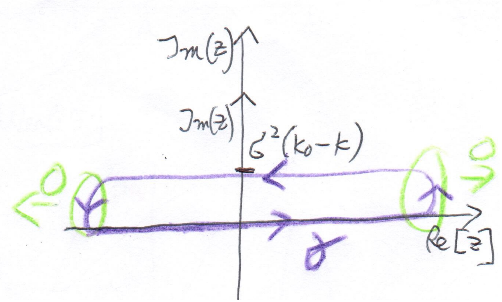
where in the third line we have introduced the Fourier space width $\sigma_k = (\sigma)^{-1}$. From line three to four we used the

Residue theorem: For the complex integral over a closed contour γ in the complex plane, we have

$$\oint_\gamma f(z)dz = 2\pi i\sum_k \mathrm{Res}[f, a_k], \tag{2.82}$$

if $f(z)$ is holomorphic everywhere in the interior of γ except at the points a_k, and $\mathrm{Res}[f, a_k]$ denotes the residue of $f(z)$ at these points.

on the following contour:



left: We pick the contour γ as shown on the left [*Please imagine the upper arm at* $-\sigma^2(k_0-k)$ *instead of* +]. Since the function $e^{-\frac{z^2}{2\sigma^2}}$ is holomorphic everywhere, we know $\oint_\gamma f(z)dz = 0$ from Eq. (2.82) and since the integral at very large or small real part of z vanishes, we can see that integrals over the two parts of the contour are equal.

To summarize we have found the

Gaussian Fourier transform pair Using $\sigma_k = 1/\sigma$, we have

$$\phi(x) = \frac{1}{(\pi\sigma^2)^{1/4}} e^{-\frac{(x-x_0)^2}{2\sigma^2}} e^{ik_0(x-x_0)}, \tag{2.83}$$

$$\tilde{\phi}(k) = \frac{1}{(\pi\sigma_k^2)^{1/4}} e^{-\frac{(k-k_0)^2}{2\sigma_k^2}} e^{-ix_0k}. \tag{2.84}$$

Now that we found the Fourier transform $\phi(k)$ of our Gaussian wavepacket, we can insert it into (2.72) to find its time evolution, which gives us:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \frac{1}{(\pi\sigma_k^2)^{1/4}} e^{-ix_0k} e^{-\sigma^2\frac{(k_0-k)^2}{2}} e^{i(kx-\frac{\hbar k^2}{2m}t)}. \tag{2.85}$$

From here we essentially do all the same tricks again, that we used to find the Fourier transform $\phi(k)$ earlier, which is mainly to reform everything again into a Gaussian for which we know the result of the integral. Let us define a complex time-dependent variable $\sigma(t)$ via

$$\sigma^2(t) = \sigma^2\left(1 + i\frac{\hbar t}{m\sigma^2}\right), \tag{2.86}$$

and let us recall that $v_0 = \hbar k_0/m$ is the velocity associated with k_0. We then write Eq. (2.85) as

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \left[\frac{1}{(\pi\sigma_k^2)^{1/4}} e^{-ix_0k} \underbrace{e^{-\sigma(t)^2\frac{(k_0-k)^2}{2}}}_{=A} \underbrace{e^{i\frac{\hbar t}{2m}\left(-2kk_0+k_0^2\right)}}_{=B}\right] \times e^{ikx}. \tag{2.87}$$

The purpose of this step, is to move the $e^{-i\frac{\hbar k^2}{2m}t}$ piece into the A term, where it looks again like forming a Gaussian. We then have to multiply in the B term to compensate any undesirable terms that have been created. Sorting these out, we reach

$$\Psi(x,t) = \underbrace{e^{i\frac{k_0v_0t}{2}}\sqrt{\frac{\sigma_k(t)}{\sigma_k}}}_{=C} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk\, \left[\frac{1}{(\pi\sigma_k(t)^2)^{1/4}} e^{-i(x_0+v_0t)k} e^{-\sigma(t)^2\frac{(k_0-k)^2}{2}}\right] \times e^{ikx}. \tag{2.88}$$

We have also defined $\sigma_k(t) = 1/\sigma(t)$ and multiplied a factor $\sqrt{\sigma_k(t)/\sigma_k}$ up front to compensate for the fact that in Eq. (2.87) the normalisation factor did contain only σ_k not $\sigma_k(t)$. At this point, we compare the Fourier transform of $\Psi(x,t)/e^{i\frac{k_0v_0t}{2}}$, which is the part in square brackets, with the Fourier transform of our original Gaussian in Eq. (2.81). We see that we reach from Eq. (2.81) to Eq. (2.88) by changing $x_0 \to x_0 + v_0t$ and $\sigma \to \sigma(t)$. If we look closely at our calculation of Eq. (2.81), we realize that it also works for complex $\sigma(t)$. Hence we can conclude that $\Psi(x,t)$ is just the original Gaussian $\Psi(x,0)$ in (2.80), if we insert transform $x_0 \to x_0 + v_0t$ and $\sigma \to \sigma(t)$, as well as multiply with the leftover pre-factors C. After that we reach

$$\Psi(x,t) = \frac{1}{(\pi[\sigma(1+i\frac{\hbar t}{m\sigma^2})]^2)^{1/4}} e^{-\frac{[x-[x_0+v_0t]]^2}{2\sigma(t)^2}} \exp\left[ik_0(x-[x_0+v_0t/2])\right]. \tag{2.89}$$

The unexpected $v_0t/2$ in the argument of the final exponential is again a symptom of the quantum mechanical phase velocity being off by a factor of two, as discussed in section 2.4.1, while the group-velocity (in the argument of the Gaussian), is as expected. We should be slightly careful comparing that with our earlier Gaussian, since the $\sigma(t)$ are complex, so we instead look at the probability density

$$|\Psi(x,t)|^2 = \frac{1}{(\pi\sigma_x(t)^2)^{1/2}} e^{-\frac{[x-[x_0+v_0 t]]^2}{\sigma_x(t)^2}}, \tag{2.90}$$

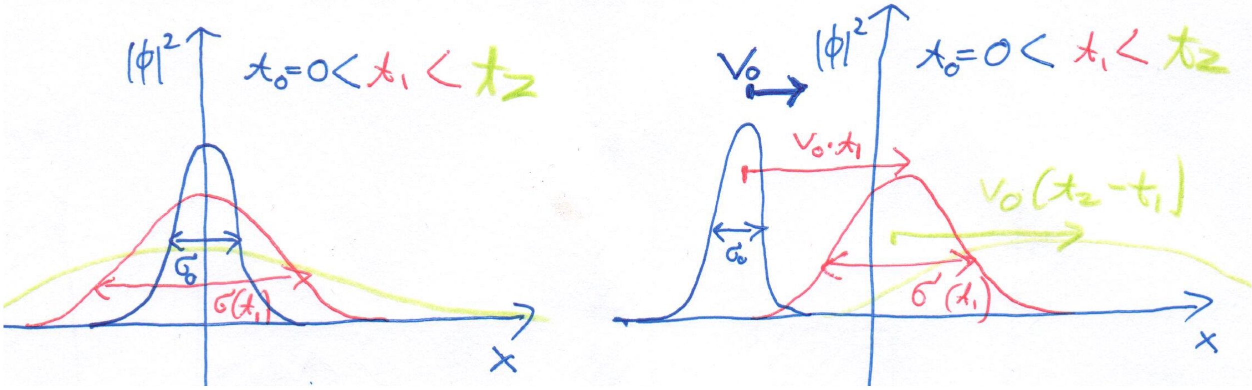
where $\sigma_x(t)$ now is a real parameter that can be interpreted as width, given below. We thus found, that as time evolves, the Gaussian wavepacket remains a Gaussian wavepacket: with a centre and width that are changing in time:

Free particle evolution Diffusion causes an increase in the width

$$\sigma_x(t) = \sqrt{\sigma^2 + \frac{\hbar^2 t^2}{m^2\sigma^2}}, \tag{2.91}$$

while the centre moves with a uniform velocity $x(t) = x_0 + \frac{p_0}{m}t = x_0 + v_0 t$.

The wavefunction thus evolves as in the drawing below: (left) $v_0 = 0$, (right) $v_0 > 0$



- The fact that $\sigma_x(t)$ increases with time is perfectly reasonable, since our initial state also has a velocity uncertainty, due to the HUP (1.47). Free particles retain their velocity, so as time increases, this initial velocity uncertainty has to convert into a position uncertainty.
- It is a very nice feature that the position uncertainty remains a Gaussian at all times.
- You can see from Eq. (2.91) that for smaller $\sigma_x(0) = \sigma$, where we initially knew better where our particle was, the time where $\sigma_x(t)$ has e.g. doubled is shorter. This is because smaller σ implies a larger initial velocity uncertainty (see dotpoint one).
- The time for doubling also becomes shorter for lower mass m, because the initial momentum uncertainty (which is fixed by Heisenberg's uncertainty relation) translates into a larger velocity uncertainty.

Fun (bonus) fact: A Gaussian wavepacket also stays a Gaussian wavepacket as long as the potential $V(x)$ has only linear+quadratic terns in its Taylor expansion over the range of $\sigma_x(t)$. All that while, its centre evolves according to the classical equations of motion. This can be exploited for a whole *class of approximation methods called semi-classical or quantum-classical methods, e.g. for quantum chemistry.*

2.7 Momentum space wavefunctions

The previous section is an example where we essentially solved the TDSE by using Fourier space. Since the Fourier representation expands a wavefunction in terms of plane waves e^{ikx} with fixed wavenumber k, and wave number is related to momentum $p = \hbar k$, the transform is more generally useful to learn more about the momentum of a particle.

Momentum space representation of a wavefunction. For a wavefunction in position space

$$\phi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp\, \tilde{\phi}(p) e^{i\frac{p}{\hbar}x} \tag{2.92}$$

we call

$$\tilde{\phi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx\, \phi(x) e^{-i\frac{p}{\hbar}x} \tag{2.93}$$

the momentum space wave function.

- This is essentially just the Fourier transform pair Eqs. (2.74) and (2.75), substituting $p = \hbar k$.
- Using (2.4), we can view this as an expansion in momentum eigenstates.
- Since the Fourier transform (2.92) uniquely specifies the function $\phi(x)$, the momentum space wavefunction $\tilde{\phi}(p)$ contains the same amount of information. Instead of specifying a position space wavefunction, we can always specify a momentum space wavefunction.
- You can show (exercise), that you can write the momentum expectation value $\langle \hat{p} \rangle$ as:

  $$\langle \hat{p} \rangle = \frac{1}{\sqrt{2\pi}} \int dp\, p |\tilde{\phi}(p)|^2. \tag{2.94}$$

  and the key component to the momentum uncertainty (1.36) as:

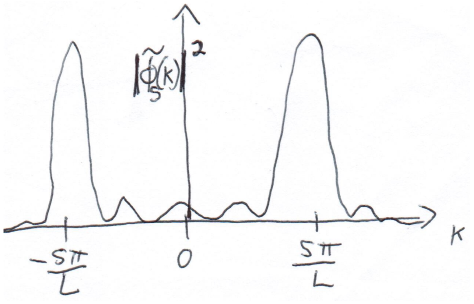
  $$\langle \hat{p}^2 \rangle = \frac{1}{\sqrt{2\pi}} \int dp\, p^2 |\tilde{\phi}(p)|^2. \tag{2.95}$$

  Comparing with the earlier expressions for $\langle \hat{x} \rangle$ using the position space wavefunction, they take the same form. All this justifies using the

Probability distribution of momentum We say that $|\tilde{\phi}(p)|^2 dp$ is the probability to find the momentum of the particle between p and $p + dp$.

Example 18, Momentum space wavefunction of particle in square well potential: We find the Fourier transform of the wavefunctions (2.18) as

$$\tilde{\phi}(k) \overset{Eq.\ (2.75)}{=} \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dx\, \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)e^{-ikx} \overset{\text{e.g. mathematica}}{=} \sqrt{\frac{a}{\pi}}\,\frac{e^{-ika}\left((-1)^{1+n}+e^{ika}\right)}{n^2\pi^2-k^2a^2}. \tag{2.96}$$



left: On the left we are drawing the resultant momentum probability density $\tilde{\phi}(p)$ for the excited state with $n = 5$. Recall from the discussion in example 13 that this essentially consists of momenta $p_\pm = \pm\hbar 5\pi/a$, corroborated by the figure (read $L = a$). Instead of sharp momenta (delta-functions $\delta(p - p_\pm)$, we see blurred peaks, since we also have to take into account that the particle is localized between 0 and a only.

2.8 The delta-function potential

In this section we want to study the delta-function potential

$$V(x) = -\alpha\delta(x). \tag{2.97}$$

This may seem badly artificial, but if you look at the drawing for the delta-function as a limit of narrower and narrower Gaussians in section 2.1, you can physically think of it as a very strong binding potential with a very narrow range, on space scales that perhaps we are not interested in. The potential then is a useful simplification and introduces some interesting tricks.

We want to thus solve the TISE $\left(\hat{T} - \alpha\delta(x)\right)\phi = E\phi$, where $\hat{T}$ is the kinetic energy operator, using our usual method of splitting space into simple regions, and looking more closely at connection points or otherwise special points. Clearly $x = 0$ is special here, while $x < 0$ and $x > 0$ are easy (there we can take the usual plane wave solutions as in the middle of regions I,II,III in e.g. section 2.2.2.

Clearly, when looking at the boundary or continuity-conditions in section 2.2.1, this is a case where the potential is not finite everywhere, hence we can only know that the wavefunction ϕ is continuous, but must allow the derivative ϕ' to be discontinuous.

However we can explicitly evaluate how much discontinuity is there, by looking at Eq. (2.14) for $x = 0$ (the location of the delta-function potential). We find

$$\left[\phi(\epsilon)' - \phi(-\epsilon)'\right] = -\frac{2m}{\hbar^2}\int_{-\epsilon}^{+\epsilon} dx\, [E + \alpha\delta(x)]\phi(x) = -\frac{2m}{\hbar^2}\left([\int_{-\epsilon}^{+\epsilon} dx E\phi(x)] + \alpha\phi(0)\right). \tag{2.98}$$

Taking the limit $\epsilon \to 0$, the term in square brackets of the last expression vanishes, since $\phi(x)$ is finite and continuous, hence we reach

$$\lim_{\epsilon\to 0}\left[\phi(\epsilon)' - \phi(-\epsilon)'\right] = -\frac{2m}{\hbar^2}\alpha\phi(0). \tag{2.99}$$

Let us keep this aside for the moment, and now look at region I ($x < 0$ excluding 0), and region II ($x > 0$ excluding 0). As before (e.g. Eq. (2.22)) we can write

$$\begin{aligned} \phi^{(I)}(x) &= Ae^{ik^{(I)}x} + Be^{-ik^{(I)}x}, \text{ for } x < 0 \\ \phi^{(II)}(x) &= Ce^{ik^{(II)}x} + De^{-ik^{(II)}x} \text{ for } x > 0. \end{aligned} \tag{2.100}$$

for $k^{(I)} = k^{(II)} = k = \sqrt{2mE}/\hbar$. Let us only look at the case $E < 0$ for now. Then $k = i\kappa$ with $\kappa = \sqrt{2m|E|}/\hbar$, hence k is <u>imaginary</u>, and (2.100) becomes:

$$\begin{aligned} \phi^{(I)}(x) &= Ae^{-\kappa x} + Be^{\kappa x}, \text{ for } x < 0 \\ \phi^{(II)}(x) &= Ce^{-\kappa x} + De^{\kappa x} \text{ for } x > 0. \end{aligned} \tag{2.101}$$

For the same reasons as in section 2.2.2, we can immediately see that $A = D = 0$, because the multiplied exponentials would diverge at infinity, and $C = B$ since the potential is symmetric. At this point, we can actually evaluate the discontinuity in the derivative on the LHS of Eq. (2.99):

$$\lim_{\epsilon\to 0}\left[\phi(\epsilon)' - \phi(-\epsilon)'\right] = \lim_{\epsilon\to 0}\left[-C\kappa e^{-\kappa\epsilon} - B\kappa e^{\kappa(-\epsilon)},\right] = 2\kappa B = 2\kappa\phi(0). \tag{2.102}$$

Combining Eq. (2.102) and Eq. (2.99) we see that $\kappa = \frac{m\alpha}{\hbar^2}$. After that, we find B by normalizing the wavefunction, and then have found the

Bound state of a delta-function potential

$$\phi(x) = \frac{\sqrt{m\alpha}}{\hbar}e^{-m\alpha|x|/\hbar^2} \tag{2.103}$$

with energy $E = -\frac{m\alpha^2}{2\hbar^2}$

- Note that this time there was no freely choosable integer n in the calculation, so there is always (only) exactly one bound state.
- We can look at scattering states with $E > 0$ by combining the techniques we used for the finite potential well in section 2.2.3 with the ones from this section. The advantage is that calculations with the delta-function potential are actually easier. See Griffith for much more on this.

Week ⑥

PHY 303 Quantum Mechanics
Instructor: Sebastian Wüster, IISER Bhopal, 2023

3 Mathematical Interlude

How that you have seen already a lot of actual quantum mechanics (physics), let us again invest one week in strengthening the mathematical formalism, by generalising what was introduced in section 1.5. Some books (e.g. Shankar) would have introduced the following directly at the beginning. Really, we will not be doing anything new, just introducing a new notation and adapting a more powerful viewpoint on the previous discussion.

3.1 Dirac notation

We introduce a notation due to Dirac. We know all quantum mechanical wavefunctions $\Psi(x)$ describing the state of a particle form the Hilbertspace, a (complete) vector space with a norm as introduced in section 1.5.4. We have also seen in section 2.7 that the same information about the particle could be contained in the momentum space wavefunction $\tilde{\Psi}(k)$. Both functions would be part of $\mathbb{L}_2$ but in terms of a different variable (x versus k) and certainly differently looking functions (compare example 18 with eigenstate $\phi_5(x)$ in the infinite square well). However they represent the same physical state of the particle. We tidy this up a bit with the following

Bra-Ket Notation We say a quantum mechanical particle is described by a vector $|\,\Psi\,\rangle$ in an abstract Hilbertspace $\mathcal{H}$. The scalar product with another vector $|\,\phi\,\rangle$ is then written as $\langle\,\phi\,|\,\Psi\,\rangle$. Earlier we had written (ϕ, Ψ). Now both pieces of the pointy "Bracket" are given a separate name $\langle\,\phi\,|$ is the "bra" vector and $|\,\Psi\,\rangle$ the "ket" vector, or simply "bra" and "ket".

- (Bonus info:) The reason $\langle\,\phi\,|$ is given a separate name, but can also be viewed as a vector, is that in formal linear algebra these also form a vector space, the dual space to our Hilbertspace, given by functionals $\int dx \phi^*(x)[\cdots]$ which map a function into a number.
- As before, we can expand any vector in terms of any basis. For example for the infinite square well potential, we can choose the basis of eigenstates (2.18). Now we write for them $|\,\phi_n\,\rangle$ or sometimes simply $|\,n\,\rangle$. The statement that we can expand any function in terms of the eigenfunctions of a Hermitian operator (here the Hamiltonian), then becomes:

$$|\,\Psi\,\rangle = \sum_n c_n |\,\phi_n\,\rangle. \tag{3.1}$$

Corresponding to the statement below (1.18), the coefficient c_k of the vector $|\,\Psi\,\rangle$ in the basis $|\,\phi_k\,\rangle$ is given by

$$c_k = \langle\,\phi_k\,|\,\Psi\,\rangle. \tag{3.2}$$

- From now on, we will consider the spatial wavefunction we had written down earlier simply as a special choice of basis for our ket-vector. In this view, choosing the position space basis $|\,x\,\rangle$ gives:

  $$\Psi(x) = \langle\,x\,|\,\Psi\,\rangle, \tag{3.3}$$

  and the momentum space basis $|\,p\,\rangle$

  $$\tilde{\Psi}(p) = \langle\,p\,|\,\Psi\,\rangle, \tag{3.4}$$

  We define these two bases via Eq. (3.3) and Eq. (3.4) and then do not have to worry how the actual basisvectors, e.g. "$|\,x\,\rangle$", actually look like. Another relation you then need for the translation from bra-ket notation to the position representation is:

  $$O(x, -i\hbar\frac{\partial}{\partial x})\Psi(x) = \langle\,x\,|\hat{O}|\,\Psi\,\rangle, \tag{3.5}$$

  where $O(x, -i\hbar\frac{\partial}{\partial x})$ is the position space representation of operator $\hat{O}$, which means that we write $\hat{O}$ in terms of $\hat{x}$ and $\hat{p}$, and then replace those with x or $-i\hbar\frac{\partial}{\partial x}$ respectively.

  If you want to worry, the momentum basis was defined in (2.4) and the position one would correspond to $|\,x\,\rangle \leftrightarrow \delta(x)$. But both of these are not nice to handle, momentum eigenstates are not normalisable and the position eigenstate is not finite and strictly not a function. Hence explicitly using these two bases is typically avoided, since we can use the relation above without doing so.

- Be warned, that the scalar product when written down in the form (f, g) given in week 1 or $\langle\,f\,|\,g\,\rangle$ introduced here somewhat hides the integration that is contained. We still have

  $$\langle\,\phi\,|\,\Psi\,\rangle = \int dx\;\phi^*(x)\Psi(x) = \int dk\;\tilde{\phi}^*(k)\tilde{\Psi}(k). \tag{3.6}$$

  In particular $\langle\,\phi\,|\,\Psi\,\rangle$ is NOT $\phi^*(x)\Psi(x)$. One nice feature of the abstract way of writing the scalar-product, is that we can still decide later whether we want to take it in position space, Fourier space, or any other space (basis). This is as for ordinary vectors, where the scalar product between two vectors also does not depend on the choice of basis.

  If you ever end up confused about the Bra-Ket notation, you can usually safely revert back to the wave-function method of writing scalar products as in (3.6).

Example 19, Flexibility of ket notation: We will later encounter new degrees of freedom that are not related to spatial coordinates, one of these is the spin. Using the ket notation we can then write e.g. one state for the spatial position of an electron $|\,\phi\,\rangle$ and another for the spin $|\,\chi\,\rangle$, but use the same notation. For the latter we cannot write a position space wavefunction such as $\chi(x)$.
Since every quantum physicist learns that $|\,\phi\,\rangle$ means "quantum state" ϕ, it also a useful conceptual tool to express this easily. You may have heard of Schrödingers cat (PHY106, week 12). Using ket notation, we can write its state at the end of the thought experiment as $|\,\Psi\,\rangle = (|\,\text{alive}\,\rangle + |\,\text{dead}\,\rangle)/\sqrt{2}$ and people still know what we mean to say.

3.2 Inner products

Earlier I had mentioned that there also is a set of axiom that defines "scalar product". We had already written the scalar product between quantum states or wavefunction using the new notation in section 3.1. Let us finally write the axioms for an

Inner product: The inner product is a map $\langle \cdots | \cdots \rangle : \mathcal{H}, \mathcal{H} \to \mathbb{C}$, which for two vectors $|\,\psi\,\rangle$, $|\,\phi\,\rangle$, $|\,\alpha\,\rangle$ and scalars c and d has the properties:

(i) $\langle\,\psi\,|\,\phi\,\rangle = \langle\,\phi\,|\,\psi\,\rangle^*$,

(ii) $\langle\,\psi\,|\,\psi\,\rangle \geq 0 \;\forall |\,\psi\,\rangle$ and $\langle\,\psi\,|\,\psi\,\rangle = 0$ only for $|\,\psi\,\rangle = |\,0\,\rangle$,

(iii) $\langle\,\psi\,|\,(c|\,\phi\,\rangle + d|\,\alpha\,\rangle) = c\langle\,\psi\,|\,\phi\,\rangle + d\langle\,\psi\,|\,\alpha\,\rangle$.

- Note that "inner product", "scalar product" and "dot product" all pretty much mean the same thing. There may be slight differences in the vector-spaces and fields involved, e.g. one calls it a dot-product if vectors are in $\mathbb{R}^n$ and the output scalar is real, but I am not convinced that these language conventions are consistently followed in physics.
- Using the new notation, we can write the norm of a vector $|\,\Psi\,\rangle$ in Hilbertspace as $\|\langle\,\Psi\,|\,\Psi\,\rangle\| = \sqrt{\langle\,\Psi\,|\,\Psi\,\rangle}$.
- You can now see that the complex conjugate that we introduced for the scalar product involving complex vectors Eq. (1.9), and the scalar product between functions (1.17) is needed to fulfill the axioms above, i.e. without it they would NOT be fulfilled (exercise).
- One consequence of the rule $\langle\,\psi\,|\,\phi\,\rangle = \langle\,\phi\,|\,\psi\,\rangle^*$, that is also easy to see from (3.6), is that for a complex scalar c, we have $\langle\,\psi\,|\,c\phi\,\rangle = c\langle\,\psi\,|\,\phi\,\rangle$, but $\langle\,c\psi\,|\,\phi\,\rangle = c^*\langle\,\psi\,|\,\phi\,\rangle$.
- You can also finally show that Eq. (1.17) is indeed an inner product.
- Just to get the hang of it, let us write down a few important statements we had seen earlier in the new notation: A basis $\{|\,\phi_n\,\rangle\}$ is orthonormal, if

  $$\langle\,\phi_n\,|\,\phi_m\,\rangle = \delta_{nm}. \tag{3.7}$$

  The TDSE (1.2) reads

  $$i\hbar\frac{d}{dt}|\,\Psi(t)\,\rangle = \hat{H}|\,\Psi(t)\,\rangle, \tag{3.8}$$

  and the TISE

  $$\hat{H}|\,\phi_n\,\rangle = E_n|\,\phi_n\,\rangle. \tag{3.9}$$

  Expectation values of an operator become

  $$\langle\hat{O}\rangle = \langle\,\Psi\,|\hat{O}|\,\Psi\,\rangle \equiv \langle\,\Psi\,|\,\hat{O}\Psi\,\rangle. \tag{3.10}$$

  If you have any other items from earlier in this lecture that you want translated into bra-ket notation, please do it for an exercise and then notify me if you think those should also be listed here.

Because we need it shortly, let use introduce a nice geometric result regarding inner product, by the name of

Schwartz inequality: for two vectors $|\,\alpha\,\rangle$, $|\,\beta\,\rangle$ we always must have

$$\langle\,\alpha\,|\,\alpha\,\rangle\langle\,\beta\,|\,\beta\,\rangle \geq |\langle\,\alpha\,|\,\beta\,\rangle|^2 \tag{3.11}$$

- Simpler example: Let us take real vectors $\mathbf{a}, \mathbf{b} \in \mathbb{R}^3$. You know that you can define the angle θ between such vectors via $\cos(\theta) = \mathbf{a} \cdot \mathbf{b}/(|\mathbf{a}||\mathbf{b}|)$. Squaring both sides we can rearrange $(\mathbf{a} \cdot \mathbf{b})^2 = |\mathbf{a}|^2|\mathbf{b}|^2 \cos(\theta)^2 \leq |\mathbf{a}|^2|\mathbf{b}|^2$, where we have expressed that $\cos^2 \leq 1$. You see that this is (3.11) for real vectors in $\mathbb{R}^3$, for a complex proof, see Griffith problem 3.5.

3.3 Matrix representation of operators

Once an arbitrary basis $|\,\phi_n\,\rangle$ of the Hilbertspace has been chosen, as usual we can express any vector $|\,\Psi\,\rangle$ in terms of this basis as

$$|\,\Psi\,\rangle = \sum_n c_n |\,\phi_n\,\rangle, \tag{3.12}$$

with complex coefficients $c_n \in \mathbb{C}$. This motivates the

Matrix representation of Operators We can write any operator $\hat{O}$ in matrix form, where the components of the matrix are

$$O_{nm} = \langle\,\phi_n\,|\hat{O}|\,\phi_m\,\rangle, \tag{3.13}$$

called matrix elements of the Operator $\hat{O}$ in the basis $|\,\phi_n\,\rangle$. The operator itself can then be written as

$$\hat{O} = \sum_{nm} O_{nm} |\,\phi_n\,\rangle\langle\,\phi_m\,|. \tag{3.14}$$

- The key advantage of matrix representations is that we can now just use the linear algebra of matrices and vectors instead of functional analysis with operators and wave functions. For example an operator applied to a wavefunction $\hat{O}\Psi(x)$, after chosing a basis, can just be constructed as

$$\hat{O}|\,\Psi\,\rangle = \left[\sum_{nm} O_{nm}|\,\phi_n\,\rangle\langle\,\phi_m\,|\right]\left[\sum_k c_k|\,\phi_k\,\rangle\right] = \sum_{nmk} O_{nm}|\,\phi_n\,\rangle \underbrace{\langle\,\phi_m\,|\,\phi_k\,\rangle}_{\delta_{mk}} = \sum_n \underbrace{\left(\sum_k O_{nk}c_k\right)}_{\equiv\tilde{c}_n} |\,\phi_n\,\rangle \tag{3.15}$$

Thus the coefficients $\tilde{c}_n$ of the state after operation with $\hat{O}$ are just found as the matrix multiplication $\underline{\underline{O}} \cdot \mathbf{c}$, where $\mathbf{c}$ is a vector with the original coefficients. We can thus use our entire arsenal of knowledge about matrices for operators. See Griffith for a lot more linear algebra revision or summary than I can provide here.

- The example in (3.15) also nicely shows that the notation $|\,\phi_n\,\rangle\langle\,\phi_m\,|$ represents <u>an operator</u>. This form is also called <u>outer product</u>.
- It is evident that the matrix representation of an operator is entirely <u>basis dependent</u>. If we change to another orthonormal basis, let's call it $|\,\psi_k\,\rangle$, we obtain another form

  $$\hat{O} = \sum_{nm} \tilde{O}_{nm} |\,\psi_n\,\rangle\langle\,\psi_m\,|. \tag{3.16}$$

  Taking scalar products from the left with $\langle\,\phi_\ell\,|\cdots$ and the right with $\cdots|\,\phi_p\,\rangle$ in both Eq. (3.14) and (3.16), you can easily show (exercise) that

  $$O_{\ell p} = \sum_{nm} \tilde{O}_{nm} \underbrace{\langle\,\phi_\ell\,|\,\psi_n\,\rangle}_{=T^*_{n\ell}} \underbrace{\langle\,\psi_m\,|\,\phi_p\,\rangle}_{\equiv T_{mp}} = \sum_{nm} T^*_{n\ell} \tilde{O}_{nm} T_{mp}. \tag{3.17}$$

  where we have defined the components T_{mp} of a <u>basis transformation matrix $\underline{\underline{T}}$</u>. With that definition, we can now write the basis transformation for the operator matrix elements simply as a matrix multiplication:

  $$\underline{\underline{O}} = \underline{\underline{T}}^\dagger \cdot \underline{\underline{\tilde{O}}} \cdot \underline{\underline{T}} \;\;\Leftrightarrow\;\; \underline{\underline{\tilde{O}}} = \underline{\underline{T}} \cdot \underline{\underline{O}} \cdot \underline{\underline{T}}^\dagger. \tag{3.18}$$

  It is easy to show, that $\underline{\underline{T}}$ is unitary: $\underline{\underline{T}}^{-1} = \underline{\underline{T}}^\dagger$ (exercise).

An important special matrix representation is the

Resolution of unity In our infinite dimensional space, the identity is

$$\mathbb{1} = \sum_{nm} \delta_{nm} |\,\phi_n\,\rangle\langle\,\phi_m\,| = \sum_{n} |\,\phi_n\,\rangle\langle\,\phi_n\,|. \tag{3.19}$$

Proof: Apply $\mathbb{1}$ as above to any arbitrary vector expanded as (3.12).

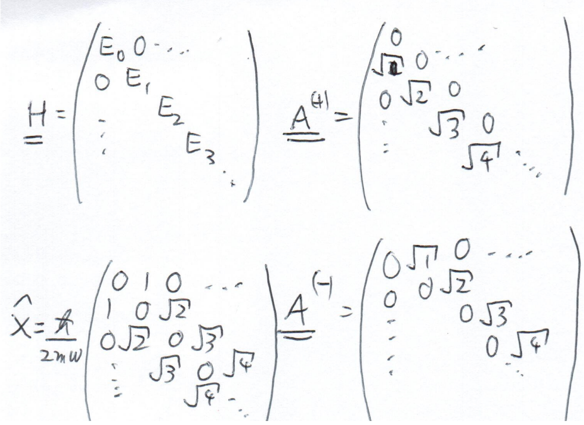
Example 20, The harmonic oscillator with matrix representations: Let us cast several operators that we used in week4 into matrix representation, using the basis $|\,\phi_n\,\rangle$ given by the eigenstates (2.65) of the Hamiltonian in Eq. (2.42) for the oscillator. The first of those is the Hamiltonian itself. That is of course <u>diagonal</u> in its eigenbasis: Using (3.13) we find matrix elements

$$H_{nm} = \langle\,\phi_n\,|\hat{H}|\,\phi_m\,\rangle \overset{Eq.\ (3.9)}{=} \langle\,\phi_n\,|E_m|\,\phi_m\,\rangle = E_m \underbrace{\langle\,\phi_n\,|\,\phi_m\,\rangle}_{=\delta_{nm}} = E_m\delta_{nm}. \tag{3.20}$$

What about the ladder operators $\hat{a}_\pm$ in Eq. (2.43)? These provide a more interesting example, and we can derive matrix elements

$$A^{(+)}_{nm} = \langle\,\phi_n\,|\hat{a}_+|\,\phi_m\,\rangle = \sqrt{m+1}\langle\,\phi_n\,|\,\phi_{m+1}\,\rangle = \sqrt{m+1}\delta_{n(m+1)}, \tag{3.21}$$

where we used Eq. (2.55). Similar to (3.21) you can show $A^{(-)}_{nm} = \sqrt{m}\delta_{n(m-1)}$.



left: <u>Since</u> we can write $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_+ + \hat{a}_-)/$ from (2.43), these two also gives us a matrix representation for $\hat{x}$. Our Matrix representations are shown in the usual table notation on the left (prefactor of $\hat{x}$ is missing a squareroot in the drawing, see formula above).

3.4 Hermitian Operators

We can now more simply define a

Hermitian operator $\hat{O}$ as one, for which the <u>matrix representation is a Hermitian matrix</u>. According to the definition in section 1.5.3 this means $O_{nm} = O^*_{mn}$, or $\underline{\underline{O}} = \underline{\underline{O}}^\dagger \equiv (\underline{\underline{O}}^T)^*$.

If we translate the definition we had given earlier in (1.24) into bra-ket notation, it can be written as

$$\langle\,\hat{O}g\,|\,f\,\rangle = \langle\,g\,|\,\hat{O}f\,\rangle \quad \big(= \langle\,g\,|\hat{O}|\,f\,\rangle\big), \tag{3.22}$$

where we temporarily use the notation $|\,\hat{O}f\,\rangle \equiv \hat{O}|\,f\,\rangle$, i.e. the "vector that is obtained after $\hat{O}$ acted on $|\,f\,\rangle$. Essentially, Eq. (3.22) tells you that

A Hermitian operator within a matrix element can act to the left onto the bra instead of acting to the right onto the ket.

- In contrast, if the operator was not Hermitian we have to define the hermitian conjugate (or adjoint) of the operator, written $\hat{O}^\dagger$, such that
$$\langle\, \hat{O}^\dagger g \,|\, f \,\rangle = \langle\, g \,|\, \hat{O} f \,\rangle, \tag{3.23}$$
is true for all g and f. (Thus a Hermitian operator is one that is its own adjoint: $\hat{O}^\dagger = \hat{O}$.
- In that case we have:
$$\langle\, \hat{O} g \,|\, f \,\rangle = \langle\, g \,|\hat{O}^\dagger|\, f \,\rangle. \tag{3.24}$$
This follows from $\langle\, \psi \,|\, \phi \,\rangle = \langle\, \phi \,|\, \psi \,\rangle^*$ (see section 3.2).

Since taking the adjoint of operators is an important operation in quantum mechanics, you must know that

Adjoint of products: of operators $\hat{A}$, $\hat{B}$, $\hat{C}$
$$\left(\hat{A}\hat{B}\hat{C}\right)^\dagger = \hat{C}^\dagger \hat{B}^\dagger \hat{A}^\dagger. \tag{3.25}$$
change their ordering.

- This is probably easiest to see using any matrix representation of the operators, see section 3.3 since in terms of matrices † consists of ^{T} and * (adjoint = transpose and complex conjugation). You should then know from the linear algebra of matrices, that a transpose of a product also implies a reordering of the matrices in the product:
$$\left(\underline{\underline{A}} \cdot \underline{\underline{B}} \cdot \underline{\underline{C}}\right)^T = \underline{\underline{C}}^T \cdot \underline{\underline{B}}^T \cdot \underline{\underline{A}}^T. \tag{3.26}$$

With our new notations and matrix representations, we can write our earlier operator eigenvalue equation (1.23) in two additional ways:

Eigenvectors of an Operator The eigenvalue problem using the bra-ket notation is
$$\hat{O}|\, \chi_n \,\rangle = o_n|\, \chi_n \,\rangle \tag{3.27}$$
or in the matrix representation
$$\underline{\underline{O}}\mathbf{c}_n = o_n \mathbf{c}_n, \tag{3.28}$$
where $\mathbf{c}_n = [c_{1n}, c_{2n}, \cdots c_{kn}, \cdots]^T$ are the coefficients in the expansion $|\, \chi_n \,\rangle = \sum_k c_{kn}|\, \phi_k \,\rangle$.

- Really all of (1.23), (3.27) and (3.27) mean the same thing and are analogous to the matrix eigenvector equations that you are used to, except that we are doing it for operators now.

Some important properties of the eigenvectors and eigenvalues of Hermitian operators/matrices:

(i) The eigenvalues of a Hermitian operator are real: From Eq. (3.27) $\langle\, \chi_n \,|\hat{O}|\, \chi_n \,\rangle = o_n \langle\, \chi_n \,|\, \chi_n \,\rangle = o_n$. But since $\hat{O}$ is Hermitian, using (3.22) we can also apply $\hat{O}$ to the left to give $\langle\, \chi_n \,|\hat{O}|\, \chi_n \,\rangle = \langle\, \chi_n \,|o_n^*|\, \chi_n \,\rangle = o_n^*$. Together $o_n = o_n^*$, which means o_n is real.

(ii) The eigenvectors of a Hermitian operator for different eigenvalues are orthogonal: Let $\hat{O}|\, \chi_n \,\rangle = o_n|\, \chi_n \,\rangle$ and $\hat{O}|\, \chi_m \,\rangle = o_m|\, \chi_m \,\rangle$ with $n \neq m$ and $o_n \neq o_m$. This time we start with $\langle\, \chi_n \,|\hat{O}|\, \chi_m \,\rangle = o_m \langle\, \chi_n \,|\, \chi_m \,\rangle$ if we operate $\hat{O}$ to the right, and $\langle\, \chi_n \,|\hat{O}|\, \chi_m \,\rangle = o_n^* \langle\, \chi_n \,|\, \chi_m \,\rangle$ if we operate it to he left. Thus $o_m \langle\, \chi_n \,|\, \chi_m \,\rangle = \underbrace{o_n^*}_{o_n} \langle\, \chi_n \,|\, \chi_m \,\rangle$, but since $o_n \neq o_m$, this can only be true if $\langle\, \chi_n \,|\, \chi_m \,\rangle = 0$. The argument no longer works if $o_n = o_m$ for $n \neq m$. However it turns out, even if eigenvectors $|\, \chi_n \,\rangle$ and $|\, \chi_m \,\rangle$ do not have to be orthogonal then, you can still always chose them such that they are.

(iii) The eigenvectors of a Hermitian operator are a basis of the Hilbertspace: I would love to prove this here, since it is central to quantum mechanics as mentioned before. However the proof for an infinite dimensional Hilbertspace requires advanced functional analysis. If you find a nice proof somewhere that you think I can include here comprehensibly, please let me know.

3.4.1 Degeneracy

We had seen in some of the above proofs, that extra care is needed whenever there are

Degenerate eigenvalues We call eigenvalues in $\hat{O}|\, \chi_n \,\rangle = o_n|\, \chi_n \,\rangle$ (twofold) degenerate, whenever $o_m = o_m$ for $n \neq m$. This means that two different eigestates $|\, \chi_n \,\rangle \neq |\, \chi_m \,\rangle$ share the same eigenvalue.
In case there are even more eigenstates, say D sharing the eigenvalue, we call it D-fold degenerate.

- The concept is exactly analogous to that of degenerate eigenvectors of a matrix. If the following discussion confuses you, please first revise the discussion for matrices, and the concept of "eigenspaces".
- Even a non-degenerate eigenfunction is only defined up to a complex phase, see (the newly added) point (iv) after the TISE (1.63). For degenerate eigenfunctions it becomes worse: Let o_m be a D-fold degenerate eigenvalue. You can easily show that any linear combination

$$|\, \xi \,\rangle = \sum_{n=0}^{D-1} c_n |\, \chi_n \,\rangle. \tag{3.29}$$

  of the normalized eigenstates $|\, \chi_n \,\rangle$ sharing that eigenvalue is itself an eigenstate of $\hat{O}$ with eigenvalue o_m (one line exercise). Here the c_n are arbitrary complex coefficients, that fulfill $1 = \sum_{n=0}^{D-1} |c_n|^2$ for $|\, \xi \,\rangle$ to be normalized. We thus do not just have eigenstates, we have an entire eigenspace. As usual, how we chose our basis in this eigenspace is our choice.

- We can even chose a non-orthogonal (but linearly independent) basis, because of which the statement (ii) above does not work directly for degenerate eigenvalues. However if we have such a basis, we can always construction and orthogonal basis from them. See literature on "Gram-Schmidt-orthogonalisation" procedure.

3.5 Schrödinger's equations in matrix form

We can finally use all the above to bring the TDSE into matrix form. Choosing a basis $\{|\,\psi_n\,\rangle\}$ that is not necessarily made of eigenstates of the Hamiltonian, the state $|\,\Psi(t)\,\rangle$ can be expanded in it at all times t. However the expansion might look different at all times, we thus have to make the expansion coefficients time dependent:

$$|\,\Psi(t)\,\rangle = \sum_n c_n(t)|\,\psi_n\,\rangle. \tag{3.30}$$

Inserting into (3.8) and multiplication from the left with $\langle\,\psi_\ell\,|\cdots$ gives us (exercise):

TDSE in matrix form for the complex coefficient vector $\mathbf{c}(t) = [c_1(t), c_2(t), \cdots]^T$ as

$$i\hbar\dot{\mathbf{c}}(t) = \underline{\underline{H}}\cdot\mathbf{c}(t), \tag{3.31}$$

or

$$i\hbar\dot{c}_\ell(t) = \sum_n \underbrace{\langle\,\psi_\ell\,|\hat{H}|\,\psi_n\,\rangle}_{=H_{\ell n}} c_n(t), \tag{3.32}$$

where $H_{\ell n}$ are the matrix elements of the Hamiltonian.

We can do the same for the TISE, but have to be careful to give the components of the basis expansion an additional index k labelling the eigenstate

$$|\,\phi_k\,\rangle = \sum_n c_n^{(k)}|\,\psi_n\,\rangle, \tag{3.33}$$

from which we find (exercise) the

TISE in matrix form for the complex coefficient vectors $\mathbf{c}^{(k)} = [c_1^{(k)}, c_2^{(k)}, \cdots]^T$ as

$$\underline{\underline{H}}\cdot\mathbf{c}^{(k)} = E_k\mathbf{c}^{(k)}, \tag{3.34}$$

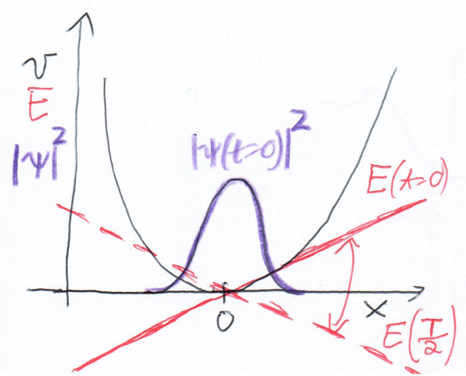
or

$$\sum_k H_{\ell n}c_n^{(k)} = E_k c_\ell^{(k)}. \tag{3.35}$$

You have already seen examples of (3.31) and (3.34) in the numerics component of assignments 2 and 3, using the discrete position basis. Let us provide one more example in another basis:

Example 21, Driven harmonic oscillator on a computer:
Let us re-consider the harmonic oscillator (section 2.3), but with a time-dependent Hamiltonian

$$\hat{H}(t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 + \underbrace{E_0 \cos(\omega t)}_{=E(t)} x. \tag{3.36}$$



left: The last part is the potential, sketched on the left, corresponding to an external time varying driving force $F = -dE(t)/dx = E_0 \cos(\omega t)$ in classical mechanics. (In the drawing $T = 2\pi/\omega$)

Let us choose the basis $|\,\phi_n\,\rangle$ given by the eigenstates (2.65) of the undriven oscillator. We had seen in example 20 that the matrix representation of the (undriven) Hamiltonian is a diagonal matrix, and that of the operator $\hat{x}$ is a matrix that has two non-zero diagonals just next to the main diagonal, let us call that matrix $\underline{\underline{X}}$.
Inserting both into Eq. (3.32) then gives us

$$i\hbar\dot{c}_\ell(t) = \sum_n [H_{\ell n}c_n(t) + X_{\ell n}c_n(t)] \quad = E_\ell c_\ell(t) + \frac{\hbar E(t)}{2m\omega}\left(\sqrt{\ell}c_{\ell-1}(t) + \sqrt{\ell+1}c_{\ell+1}\right). \tag{3.37}$$

We could now solve the coupled system of ordinary differential equations (ODEs) (3.37) quite easily on a computer. Note c_{-1} does not exist, if it would appear on the RHS, insert 0.

Week ⑦

PHY 303 Quantum Mechanics

Instructor: Sebastian Wüster, IISER Bhopal, 2023

These notes are provided for the students of the class above only. There is no guarantee for correctness, please contact me if you spot a mistake.

3.6 The generalized statistical interpretation

We can now recast the basis of quantum mechanics discussed in week2 in the new language developed above. The following is also called the postulates of quantum mechanics. Here "postulates" means we assume this is true, and then develop all the rest mathematically from this input. There is presently no deeper explanation of why these postulate are as they are, they are simply the ones from which we can develop a theory that correctly has described every single experimental observation since it invention.

For reference, we show the postulates side-by-side with corresponding axioms of classical mechanics (see PHY305) in table 3.

S.No.	Classical mechanics	Quantum mechanics
I	The mechanical state of a particle at time t is given by a pair of phase-space coordinates $[x(t), p(t)]$	The mechanical state of a particle is represented by a normalized vector $|\,\Psi(t)\,\rangle$ in a Hilbertspace.
II	Observable quantities are represented by a function $O(x, p)$ on phase space.	Observable quantities are represented by Hermitian operators $\hat{O}$.
III	An ideal measurement of $O(x, p)$ will give the result O with certainty.	If we measure the observable $\hat{O}$ we find the result o_n with probability $p_n = |c_n|^2$ if the state of the particle had the expansion $|\,\Psi\,\rangle = \sum_n c_n |\,\phi_n\,\rangle$ in terms of eigenstates $|\,\phi_n\,\rangle$ of $\hat{O}$.
IV	When measuring observable O, the state of the particle x, p is not affected.	After a measurement with the result o_k (where $\hat{O}|\,\phi_n\,\rangle = o_n|\,\phi_n\,\rangle$) the state of the particle is collapsed onto the eigenstate $|\,\phi_k\,\rangle$, i.e. $|\,\Psi\,\rangle = |\,\phi_k\,\rangle$, such that any immediately repeated measurement subsequently gives o_k with probability $p_k = 1$.
V	The state variables change according to Hamilton's equations $\dot{x} = \frac{\partial \mathcal{H}}{\partial p}$ and $\dot{p} = -\frac{\partial \mathcal{H}}{\partial x}$. (think Newton's equations)	The state vector $|\,\Psi(t)\,\rangle$ evolves according to the TDSE (3.8).

Table 1: The quantum mechanical postulates (right column), compared with the state of affairs in classical mechanics.

- We have focussed on the mechanical degrees of freedom position and momentum above, but the quantum-column pertains more general to any observables.
- The above uses some terminology you might only learn later this semester in PHY303 classical mechanics, such as "phase space" and Hamilton's equations.
- The quantum mechanical time evolution postulate V only applies if we are not dealing with the time-evolution that gives rise to a measurement process, for which we need to invoke postulate IV additionally. This remains a deeply unsatisfactory feature of the formalism, see e.g. lecture PHY635 (decoherence).

3.7 The generalized uncertainty principle

We had already earlier stated the Heisenberg uncertainty principle (1.47), but without proof. Now comes the proof, for a more general scenario. Consider two quantum mechanical observables, represented by <u>Hermitian</u> operators $\hat{A}$ and $\hat{B}$ as discussed in the previous section. The squared uncertainty for each of them, in state $|\,\Psi\,\rangle$, starting with definition (1.42), using the new bra-ket notation and then reverting to the original definition of the standard deviation (1.8) can be written as e.g.

$$\sigma_A^2 = \langle\,\Psi\,|(\hat{A}-\langle\hat{A}\rangle)^2|\,\Psi\,\rangle \overset{Eq.\ (3.22)}{=} \langle\,(\hat{A}-\langle\hat{A}\rangle)\Psi\,|\,(\hat{A}-\langle\hat{A}\rangle)\Psi\,\rangle = \langle\,f\,|\,f\,\rangle, \tag{3.38}$$

where in the last step we introduced the new state $|\,f\,\rangle = (\hat{A}-\langle\hat{A}\rangle)|\,\Psi\,\rangle$. Similarly we can write the squared uncertainty of $\hat{B}$ as $\sigma_B^2 = \langle\,g\,|\,g\,\rangle$ using $|\,g\,\rangle = (\hat{B}-\langle\hat{B}\rangle)|\,\Psi\,\rangle$. Multiplying the two, we find

$$\sigma_A^2\sigma_B^2 = \langle\,f\,|\,f\,\rangle\langle\,g\,|\,g\,\rangle \overset{Eq.\ (3.11)}{\geq} |\langle\,f\,|\,g\,\rangle|^2. \tag{3.39}$$

For any complex number z we have $|z|^2 = \mathfrak{Re}[z]^2 + \mathfrak{Im}[z]^2 \geq \mathfrak{Im}[z]^2 = \left[\frac{1}{2i}(z-z^*)\right]^2$. Using this on the complex number $z = \langle\,f\,|\,g\,\rangle$, we thus can write

$$\sigma_A^2\sigma_B^2 \geq \left[\frac{1}{2i}(\langle\,f\,|\,g\,\rangle - \langle\,g\,|\,f\,\rangle)\right]^2. \tag{3.40}$$

Re-inserting our earlier definitions of $|\,f\,\rangle$ and $|\,g\,\rangle$, you can show (see Griffith p 109), that

$$\langle\,f\,|\,g\,\rangle = \langle\hat{A}\hat{B}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle \text{ and } \langle\,g\,|\,f\,\rangle = \langle\hat{B}\hat{A}\rangle - \langle\hat{A}\rangle\langle\hat{B}\rangle \tag{3.41}$$

hence $\langle\,f\,|\,g\,\rangle - \langle\,g\,|\,f\,\rangle = \langle[A,B]\rangle$ using the

Commutator of operators: $\hat{A}$ and $\hat{B}$, which is another operator

$$[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{3.42}$$

- We had seen the first commutator earlier in Eq. (2.45).

- We know the "ordering of operators matters". The commutator is what you have to add, if you want to re-order them anyway, i.e.

$$\hat{A}\hat{B} = \hat{B}\hat{A} + \big[\hat{A}, \hat{B}\big]. \tag{3.43}$$

Using the commutator, we can turn (3.40) into the

Generalized uncertainty principle The uncertainty product of two operators is given by

$$\sigma_A \sigma_B \geq \sqrt{\left(\frac{1}{2i}\langle[\hat{A}, \hat{B}]\rangle\right)^2}, \tag{3.44}$$

through the commutator $\big[\hat{A}, \hat{B}\big]$ of the operators.

Example 22, Position-momentum uncertainty principle: We can immediately apply this to the position operator $\hat{A} = \hat{x}$ and the momentum operator $\hat{B} = \hat{p}$. Since we already know their commutator is $\big[\hat{x}, \hat{p}\big] = i\hbar$, see Eq. (2.46). Inserting this, we straightaway recover Eq. (1.47).

- You will later use Eq. (3.44) to derive many further uncertainty relations. Those involve angular momentum operators, spin, amplitude and phase of electromagnetic fields, current and phase of superconducting circuits etc.

We had seen above, that the commutator of operators takes a central role in quantum mechanics. For that reason, the following rules are frequently useful:

Commutator identities: We trivially have $\big[\hat{A}, \hat{B}\big] = -\big[\hat{B}, \hat{A}\big]$. Nextly, the commutator is bi-linear (linear in both arguments, which means

$$\begin{aligned}
\big[\hat{A}, \hat{B} + \hat{C}\big] &= \big[\hat{A}, \hat{B}\big] + \big[\hat{A}, \hat{C}\big], \\
\big[\hat{A} + \hat{B}, \hat{C}\big] &= \big[\hat{A}, \hat{C}\big] + \big[\hat{B}, \hat{C}\big].
\end{aligned} \tag{3.45}$$

For commutators involving operator products, you can use

$$\big[\hat{A}, \hat{B}\hat{C}\big] = \big[\hat{A}, \hat{B}\big]\hat{C} + \hat{B}\big[\hat{A}, \hat{C}\big]. \tag{3.46}$$

Finally, there is the Jacobi-identity for nested commutators

$$\big[\hat{A}, \big[\hat{B}, \hat{C}\big]\big] + \big[\hat{B}, \big[\hat{C}, \hat{A}\big]\big] + \big[\hat{C}, \big[\hat{A}, \hat{B}\big]\big] = 0. \tag{3.47}$$

Proofs: self exercise.

3.8 Compatibility of observables

One conclusion from the generalized uncertainty principle (3.44) is, that when two operators $\hat{A}$ and $\hat{B}$ commute, which means that $\left[\hat{A}, \hat{B}\right] = 0$, there is no restriction on the uncertainty-product of the corresponding observables and it actually is possible to know the physical quantities A and B perfectly at the same time.

Example 23, Free particle states revisited: Consider for example the free particle with Hamiltonian $\hat{H} = \hat{p}^2/(2m)$ and momentum operator $\hat{p}$. If we ignore for the moment our unhappiness with the states Eq. (2.4) not being normalizable, we realize that they are associated with a well defined momentum p and at the same time eigenstates of the Hamiltonian with energy $E = p^2/(2m)$. If we evaluate the commutator, we trivially find $\left[\hat{p}, \hat{H}\right] = 0$, supporting the link above.

There is a simple reason from linear algebra, why operators that commute allow some observables to be well defined simultanouesly:

Simultaneous diagonalisability: If two operators commute $\left[\hat{A}, \hat{B}\right] = 0$, there exist a set of Hilbertspace vectors $|\, v_n \,\rangle$ (forming a basis) that are eigenvectors of both operators:

$$\hat{A}|\, v_n \,\rangle = a_n|\, v_n \,\rangle, \tag{3.48}$$

$$\hat{B}|\, v_n \,\rangle = b_n|\, v_n \,\rangle. \tag{3.49}$$

Proof: Linear Algebra courses or books.

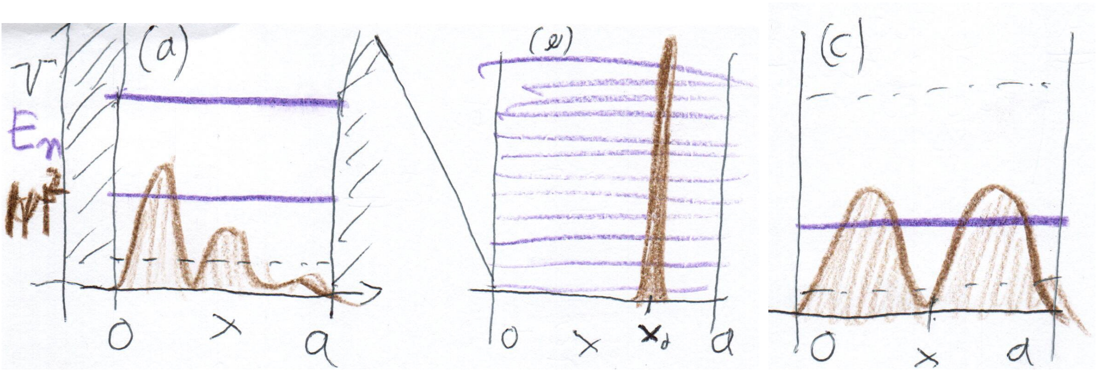
- We thus call physical observables $\hat{A}$ and $\hat{B}$ with $\left[\hat{A}, \hat{B}\right] = 0$ compatible: There exist states $|\, \Psi \,\rangle$ which may be eigenstates of both, such that a measurement of either gives a well defined answer without uncertainty, according to postulate III in table 3. In contrast, if $\left[\hat{A}, \hat{B}\right] \neq 0$ they are called incompatible, since (3.44) precludes them simultaneously having no uncertainty.
- In one dimension it is a bit difficult to find examples of compatible observables beyond example 23 because there is not that many different observables. We will reconsider compatibility of observables extensively in chapter 4, dealing with 3D problems.
- The statement in the box above directly generalized to a set of N observables $\{\hat{O}_1, \hat{O}_2, \cdots, \hat{O}_N\}$. If (and only if) all mutual commutators vanish $\left[\hat{O}_k, \hat{O}_\ell\right] = 0$ for all k, ℓ there will be a set of eigenfunctions $|\, v_n \,\rangle$ that are simultaneously eigenfunctions of all these operators.

It is easier to find examples of incompatible observables

Example 24, Sequentially measuring incompatible observables: This example should illustrate section 3.8 and table 3. Consider a particle in the infinite square well potential as in section 2.2.1. Let its initial state be

$$|\,\Psi(t=0)\,\rangle = \frac{1}{\sqrt{2}}\left(|\,\phi_2\,\rangle + |\,\phi_3\,\rangle\right), \tag{3.50}$$

shown in panel (a), using infinite square well eigenstates $|\,\phi_n\,\rangle$ in Eq. (2.18).



- According to the measurement postulate III in table 3, if we now measure the energy, we can only either find E_2 with probability $p_2 = |\frac{1}{\sqrt{2}}|^2 = \frac{1}{2}$ or E_3 with probability $p_3 = \frac{1}{2}$. If instead we measure the position, many results $x_0 \in [0\,a]$ are possible, with probability $|\langle\,x\,|\,\Psi\,\rangle|^2 dx = |\Psi(x)|^2 dx$ for a finding in $[x_0 \;\; x_0 + dx]$. (To cast the position space representation in terms of postulate III, think of the states as $|\,\Psi\,\rangle = \int dx\,\underbrace{\langle\,x\,|\,\Psi\,\rangle}_{\Psi(x)}|\,x\,\rangle$).

- Suppose at time t_1 we measure that the position is x_0 up to measurement resolution dx. According to the collapse postulate IV, just after that measurement, the wavefunction is highly localized around x_0 as shown in (b). Such a state can of course again be expanded in terms of our basis $|\,\phi_n\,\rangle$. Let us approximate the post-measurement state by $\Psi(x, t_1) \approx \delta(x - x_0)$. Using (3.2), we can write

$$\Psi(x, t_1) = \sum_n c_n \phi_n(x), \;\text{ with } c_n = \int dx\; \phi_n^*(x)\delta(x - x_0) = \phi_n^*(x_0). \tag{3.51}$$

  It is clear from the form of $\phi_n^*(x_0)$ that a large number of c_n are nonzero. We have thus now changed the number and probability of available results of a measurement of energy (available results for an energy measurement are shown as violet lines in the drawing). The position measurement has changed the state of the system.

- Finally, let us measure the energy at time $t_2 > t_1$ and suppose we find it is E_2, panel (c). This again changes the position space probability distribution, which now is no longer localized, but is shown in brown. But directly after this measurement, only a single energy result can be found (violet line).

3.8.1 The energy-time uncertainty relation

There is also an uncertainty relation between energy and time, that we already glimpsed in PHY106. But here, and it its interpretation, we have to be very careful. It is altogether a very different relation from Eq. (3.44). We cannot simply apply (3.44) to energy and time, since time is not an operator. There is also no such thing as a "measurement of the time of a particle". Time, in the TDSE formalism, is simply an external parameter that governs the time-evolution.

So before having any chance to write or understand an energy-time uncertainty relation, we first have to make clear what we mean by "time uncertainty". In contrast for energy this is easy, we can use (1.42) and apply it to the Hamiltonian to find $\Delta E = \sigma_E = \sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2}$ as a perfectly fine definition of energy uncertainty. So what with a time uncertainty?

We shall be referring to as Δt is in fact the "characteristic time-scale" on which the expectation value of an observable $\hat{Q}(t)$ is changing, if the Hamiltonian is $\hat{H}$ and the state $|\,\Psi(t)\,\rangle$ changing in time. Then

$$\frac{d}{dt}\langle \hat{Q} \rangle = \frac{d}{dt}\langle\, \Psi(t)\,|\hat{Q}(t)|\,\Psi(t)\,\rangle = \left(\frac{\partial}{\partial t}\langle\, \Psi\,|\right)\hat{Q}|\,\Psi\,\rangle + \langle\, \Psi\,|\frac{\partial \hat{Q}}{\partial t}|\,\Psi\,\rangle + \langle\, \Psi\,|\hat{Q}\left(\frac{\partial}{\partial t}|\,\Psi\,\rangle\right). \tag{3.52}$$

For the time-derivatives of wavefunctions, we can use the TDSE $i\hbar\frac{\partial}{\partial t}|\,\Psi\,\rangle = \hat{H}|\,\Psi\,\rangle$ and its conjugate $-i\hbar\frac{\partial}{\partial t}\langle\, \Psi\,|\hat{H} = \langle\, \Psi\,|\hat{H}$, hence:

$$\begin{aligned}\frac{d}{dt}\langle \hat{Q} \rangle &= -\frac{1}{i\hbar}\langle\, \Psi\,|\hat{H}\hat{Q}|\,\Psi\,\rangle + \langle\, \Psi\,|\frac{\partial \hat{Q}}{\partial t}|\,\Psi\,\rangle + \frac{1}{i\hbar}\langle\, \Psi\,|\hat{Q}\hat{H}|\,\Psi\,\rangle \\ &= \frac{1}{i\hbar}\langle\, \Psi\,|\big[\hat{Q},\hat{H}\big]|\,\Psi\,\rangle + \langle\, \Psi\,|\frac{\partial \hat{Q}}{\partial t}|\,\Psi\,\rangle. \end{aligned} \tag{3.53}$$

While we have not yet reached where we are heading for the uncertainty principle, this already tells us the

Time evolution of an expectation value is given by

$$\frac{d}{dt}\langle \hat{Q} \rangle = \frac{1}{i\hbar}\langle \big[\hat{Q},\hat{H}\big] \rangle + \langle \frac{\partial \hat{Q}}{\partial t} \rangle. \tag{3.54}$$

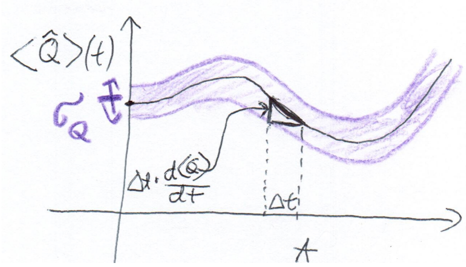
In particular $\langle \hat{Q} \rangle$ remains constant ("Q is conserved") if $\hat{Q}$ does not explicitly depend on time and commutes with the Hamiltonian.

Assuming $\hat{Q}$ does not explicitly depend on time and hence $\frac{\partial \hat{Q}}{\partial t} = 0$, we can now insert Eq. (3.54) into the RHS of Eq. (3.44) for the uncertainty product of $\hat{H}$ and $\hat{Q}$:

$$\sigma_H^2 \sigma_Q^2 \geq \left(\frac{1}{2i}\langle \big[\hat{H},\hat{Q}\big] \rangle\right)^2 \overset{Eq.\ (3.54)}{=} \left(\frac{\hbar}{2}\right)^2 \left(\frac{\partial \langle \hat{Q} \rangle}{\partial t}\right)^2 \tag{3.55}$$

Now we call the uncertainty in energy $\Delta E = \sigma_H$ and define the

Characteristic time for change of an observable associated with $\hat{Q}$ as



left:

$$\Delta t = \frac{\sigma_Q}{|d\langle Q\rangle/dt|}. \tag{3.56}$$

Why this makes sense is visualized on the left: This is the time it takes for $\langle Q\rangle$ to change by the uncertainty (for shorter times we cannot "discern" the change properly).

With this definition we can finally formulate the

Energy-time uncertainty relation as

$$\Delta E \Delta t \geq \frac{\hbar}{2}. \tag{3.57}$$

- This looks nicely similar to the position-momentum relation (1.47), particular considering that in special relativity energy and momentum as well as position and time are treated on equal footing. However it should be clear from this section, that it is very differently derived and thus has a quite different meaning.

Example 25, Eigenstates versus superpositions: (a) Consider an energy eigenstate $\Psi(x,t) = \phi(x)e^{-iEt/\hbar}$. Here the energy uncertainty vanishes $\Delta E = 0$, see section 1.6.5 and no expectation value will ever change in time since the state is stationary. Hence $d\langle Q\rangle/dt = 0$ and, using (3.56), the characteristic timescale $\Delta t \to \infty$, which is also required from (3.57). This case is similar to considering a momentum eigenstate in the position-momentum HUP (1.47).
(b) Consider a superposition of two infinite square well eigenstates such as in example 14

$$\Psi(x,t) = \left[\phi_1(x)e^{-iE_1 t/\hbar} + \phi_2(x)e^{-iE_2 t/\hbar}\right]/\sqrt{2}. \tag{3.58}$$

We focus on the expectation value of position $\langle x\rangle(t) = \langle\, \phi_1 \,|\hat{x}|\, \phi_2 \,\rangle e^{i(E_1-E_2)t/\hbar} + \text{c.c.}$ We can take the period of its oscillations $T = 2\pi\hbar/|E_1 - E_2|$ as characteristic time-scale $\Delta t = T$ and evaluate $\Delta E = \sigma_H = \sqrt{(E_1^2 + E_2^2)/2 - [(E_1+E_2)/2]^2} = |E_1 - E_2|/2$ (exercise), which indeed gives $\Delta E \Delta t = \pi\hbar \geq \frac{\hbar}{2}$.

3.9 Quantum dynamics and time evolution pictures

Further reading: See Griffith (3rd edition) chapter 6 or e.g. Sakurai, "Modern quantum mechanics", chapter 2.1 and 2.2.

We had already seen that the time-dependent Schrödinger equation (3.8) is a PDE of first order in time, that evolves a quantum state from time $t = 0$ where it is the initial state $|\,\Psi(0)\,\rangle$ to the state $|\,\Psi(t)\,\rangle$ at a later time t.

Since this process thus maps one state onto another, we can think of it as an operator, see (1.21). We shall now find the precise form of the operator, let us write solutions of the TDSE in another form than we usually do. You can convince yourself by insertion, that

$$|\,\Psi(t)\,\rangle = e^{-i\frac{\hat{H}}{\hbar}t}|\,\Psi(0)\,\rangle \tag{3.59}$$

solves the TDSE. Here we have used a

Function of an operator: If we encounter $f(\hat{O})$, where $f(x)$ is a function and $\hat{O}$ is an operator, we can define this by writing the Taylor series of the function $f(x) = \sum_{n=0}^{\infty} c_n x^n$, and then inserting the operator into it:

$$f(\hat{O}) = \sum_{n=0}^{\infty} c_n \hat{O}^n. \tag{3.60}$$

For the case above, we thus use $e^{-i\frac{\hat{H}}{\hbar}t} = \sum_{n=0}^{\infty}\left(\frac{-it}{\hbar}\right)^n \frac{1}{n!}\hat{H}^n$. Using this, you can for example easily convince yourself that $\frac{d}{dt}e^{-i\frac{\hat{H}}{\hbar}t} = e^{-i\frac{\hat{H}}{\hbar}t}\left(-i\frac{\hat{H}}{\hbar}\right)$, which is all you need to show that (3.59) solves the TDSE. We thus have found the

Time evolution operator, also called <u>propagator</u> for the case of a time-independent Hamiltonian

$$\hat{U}(t,0) = e^{-i\frac{\hat{H}}{\hbar}t}, \tag{3.61}$$

defined such that

$$|\,\Psi(t)\,\rangle = \hat{U}(t,0)|\,\Psi(0)\,\rangle. \tag{3.62}$$

- You can easily see that this is fully equivalent to Eq. (1.71) which you know since a long time. Let $|\,\Psi(0)\,\rangle = \sum_n c_n(0)|\,\phi_n\,\rangle$, where $\hat{H}|\,\phi_n\,\rangle = E_n|\,\phi_n\,\rangle$, then

$$\begin{aligned}|\,\Psi(t)\,\rangle = |\,\Psi(0)\,\rangle &= \sum_n c_n(0)e^{-\frac{i}{\hbar}\hat{H}t}|\,\phi_n\,\rangle = \sum_n c_n(0)\left[\sum_{k=0}^{\infty}\frac{\left(-\frac{i}{\hbar}\hat{H}t\right)^k}{k!}\right]|\,\phi_n\,\rangle \\ &= \sum_n c_n(0)\left[\sum_{k=0}^{\infty}\frac{\left(-\frac{i}{\hbar}E_n t\right)^k}{k!}\right]|\,\phi_n\,\rangle = \sum_n c_n(0)e^{-\frac{i}{\hbar}E_n t}|\,\phi_n\,\rangle,\end{aligned} \tag{3.63}$$

  which is Eq. (1.71).
- The operator us <u>unitary</u>, which means $\hat{U}^{-1} = \hat{U}^\dagger$. Proof:

$$\hat{U}(t,0)\hat{U}^\dagger(t,0) = e^{-i\frac{\hat{H}}{\hbar}t}e^{i\frac{\hat{H}^\dagger}{\hbar}t} \overset{\hat{H}^\dagger=\hat{H}}{=} e^{-i\frac{\hat{H}}{\hbar}t+i\frac{\hat{H}}{\hbar}t} = \mathbb{1}. \tag{3.64}$$

We could have shown this as a requirement for the state to preserve its normalisation: Suppose $\langle\, \Psi(0) \,|\, \Psi(0) \,\rangle = 1$. Now $\langle\, \Psi(t) \,|\, \Psi(t) \,\rangle = \langle\, \Psi(0) \,|\hat{U}^\dagger(t,0)\hat{U}(t,0)|\, \Psi(0) \,\rangle$. For the latter to be also one, we require $\hat{U}^\dagger(t,0)\hat{U}(t,0) = \mathbb{1}$. People thus also use unitary quantum dynamics synonymous with normalisation preserving quantum dynamics.

- All the arguments above work the same if we change the initial time from $t = 0$ to t_0. We then call the evolution operator $\hat{U}(t, t_0)$. You can show that it fulfills $\hat{U}(t_2, t_0) = \hat{U}(t_2, t_1)\hat{U}(t_1, t_0)$ for any $t_2 > t_1 > t_0$, which is perfectly logical.
- For time-dependent $\hat{H}(t)$, the time-evolution operator becomes significantly more complicated, we defer this to next semester.
- The differentiation that lead us to definition (3.61) (see above that definition), can be rewritten as

$$i\hbar\frac{d}{dt}\hat{U}(t,0) = \hat{H}\hat{U}(t,0). \tag{3.65}$$

We see that the time-evolution operator fulfils an equation of pretty much the same structure as the TDSE, but being an equation for an operator.

Example 26, Numerical solution of TDSE using the propagator: You can show that if $\hat{U}(t,0) = e^{-i\frac{\hat{H}}{\hbar}t}$ then the same relation hold for the respective matrix representations of the operators involved: $\underline{\underline{U}}(t_1, t_0) = e^{-i\frac{\underline{\underline{H}}}{\hbar}(t_1 - t_0)}$, where we use the matrix exponential $e^{\underline{\underline{A}}} = \sum_{n=0}^{\infty} \underline{\underline{A}}^n/n!$. To "propagate" a quantum state over an small discrete time-step Δt, we thus require $\underline{\underline{U}}(\Delta t) \equiv \underline{\underline{U}}(t_0 + \Delta t, t_0) = e^{-i\frac{\underline{\underline{H}}}{\hbar}\Delta t}$. If we know the matrix representation of $\underline{\underline{H}}$, say for the driven oscillator as in example 21, we can calculate $\underline{\underline{U}}(\Delta t)$ once, and then just repeatedly multiply it onto the state vector to calculate a solution of the TDSE.

3.9.1 Different pictures of time-evolution

Note that to describe reality (=experiments), all we need to know is the time-dependence of expectation values of observables $\hat{Q}$ that we intend to measure. Let us write one such, in the state $|\, \Psi(t) \,\rangle$ as:

$$\langle\hat{Q}\rangle(t) = \langle\, \Psi(t) \,|\hat{Q}|\, \Psi(t) \,\rangle \overset{Eq.\ (3.62)}{=} \langle\, \Psi(0) \,|\, \underbrace{\hat{U}^\dagger(t,0)\hat{Q}\hat{U}(t,0)}_{\equiv\hat{Q}(t)} \,|\, \Psi(0) \,\rangle. \tag{3.66}$$

In the second equality we have used the time-evolution operator, and then defined a time dependent operator $\hat{Q}(t)$. Since we only care about $\langle\hat{Q}\rangle(t)$, this makes clear that mathematically we have the choice, to use (i) time-dependent quantum states and time-independent operators, or (ii) time-independent states (initial states) and time-dependent operators. Both approaches have different advantages. We call (i) the Schrödinger picture. We have used that one so far, and will also continue using it for most of this course. We call (ii) the Heisenberg picture. It has some formal advantages, in that it makes links between classical mechanics (PHY 305) and quantum mechanics more apparent, and can also be useful for practical calculations of more complex problems. We thus spend one section looking at it in a bit more detail.

Schrödinger picture: In order not to get confused when we are dealing with the Heisenberg picture, we now add subscripts $_S$ to all variables that are handled in the Schrödinger picture. We thus know that operators $\hat{Q}_S$ are time-independent and states $|\,\Psi_S\,\rangle$ evolve according to the TDSE

$$i\hbar\frac{d}{dt}|\,\Psi_S(t)\,\rangle = \hat{H}_S|\,\Psi_S(t)\,\rangle. \tag{3.67}$$

Heisenberg picture: Now we shall use subscripts $_H$ for states or operators in the Heisenberg picture. We had already defined the time-evolving Heisenberg picture operator in (3.66), hence

$$\hat{Q}_H(t) = \hat{U}^\dagger(t,0)\hat{Q}_S\hat{U}(t,0). \tag{3.68}$$

Let us assume the Schrödinger picture operator $\hat{Q}_S$ to not explicitly depend on time, which applies to most cases discussed so far. An important immediate consequence, is that at time $t = 0$, the Schrödinger picture operator $\hat{Q}_S$ and the Heisenberg picture operator $\hat{Q}_H(t)$ are identical $\hat{Q}_H(0) = \hat{Q}_S$. For the later time-evolution of $\hat{Q}_H(t)$ let us find a new equation of motion by:

$$\begin{aligned}\frac{d}{dt}\hat{Q}_H(t) &\overset{Eq.\ (3.68)}{=} \left(\frac{d}{dt}\hat{U}^\dagger(t,0)\right)\hat{Q}_S\hat{U}(t,0) + \hat{U}^\dagger(t,0)\hat{Q}_S\left(\frac{d}{dt}\hat{U}(t,0)\right)\\ &\overset{Eq.\ (3.65)}{=} -\frac{1}{i\hbar}\hat{U}^\dagger(t,0)\hat{H}\hat{Q}_S\hat{U}(t,0) + \frac{1}{i\hbar}\hat{U}^\dagger(t,0)\hat{Q}_S\hat{H}\hat{U}(t,0).\\ &\overset{Eq.\ (3.64)}{=} -\frac{1}{i\hbar}\hat{U}^\dagger(t,0)\hat{H}\underbrace{\hat{U}\hat{U}^\dagger}_{=\mathbb{1}}\hat{Q}_S\hat{U}(t,0) + \frac{1}{i\hbar}\hat{U}^\dagger(t,0)\hat{Q}_S\underbrace{\hat{U}\hat{U}^\dagger}_{=\mathbb{1}}\hat{H}\hat{U}(t,0).\end{aligned} \tag{3.69}$$

In the last line, we have used the common trick, to insert $\mathbb{1}$ in the form shown, at locations where it helps us subsequently. Namely we realize that we can now write the right hand side as:

$$\frac{d}{dt}\hat{Q}_H(t) = -\frac{1}{i\hbar}\left[\hat{U}^\dagger(t,0)\hat{H}\hat{U}(t,0), \hat{U}^\dagger(t,0)\hat{Q}_S\hat{U}(t,0)\right]. \tag{3.70}$$

Using Eq. (3.68) we can now write the

Heisenberg equation for the time evolution of any operator in the Heisenberg picture, as

$$i\hbar\frac{d}{dt}\hat{Q}_H(t) = \left[\hat{Q}_H, \hat{H}_H\right]. \tag{3.71}$$

- Note that the Heisenberg equation applies also to $\hat{Q} = \hat{H}$, i.e. the Hamiltonian itself. We then trivially obtain $i\hbar\frac{d}{dt}\hat{H}_H(t) = 0$, implying $\hat{H}_H(t) = \hat{H}_H(0) = \hat{H}_S(0)$. We could thus drop the subscript $_H$ in (3.71).

Example 27, Harmonic oscillator in the Heisenberg picture: Let us reconsider the harmonic oscillator, with Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2. \tag{3.72}$$

Using the known commutator (2.46), and the rule (3.46), you can find the Heisenberg equation of motion for the position operator $\hat{x}_H$ and momentum operator $\hat{p}_H$ in the Heisenberg picture (exercise):

$$\frac{d}{dt}\hat{x}_H(t) = \hat{p}_H(t)/m \quad \text{and} \quad \frac{d}{dt}\hat{p}_H(t) = -m\omega^2\hat{x}_H(t). \tag{3.73}$$

These really look like the classical equations of motion for the oscillator, expect that x and p are now operators. It turns out that these equations can then be solved using more or less the same tricks with which you solve them in the classical case.

You have seen in both pictures, that the time-dependence is ultimately due to the Hamiltonian. It turns out that there are not only two, but many pictures, since we can now mix both approaches: We can do the math such that the time-dependence due to some part of the Hamiltonian is encapsulated in the quantum sates, and the time-dependence due to another part of the Hamiltonian in the operators. This is called the interaction picture, and we shall encounter it again in PHY304 QM-II, when we consider time-dependent perturbation theory.

Week ⑧

PHY 303 Quantum Mechanics
Instructor: Sebastian Wüster, IISER Bhopal, 2023

These notes are provided for the students of the class above only. There is no guarantee for correctness, please contact me if you spot a mistake.

4 Quantum mechanics in three dimensions

So far we have dealt with one spatial dimension x only (1D), for simplicity and ease of notation. Of course the real world is 3D. Luckily, most of what we learnt so far straightforwardly generalizes from 1D to 3D, as we shall discuss in this “week” segment. New physics that comes in when we go to 3D is that of angular momentum (which does not exist in 1D). We will discuss angular momentum in the subsequent week, in the context of the Hydrogen atom, which will be the main focus of this chapter.

4.1 Higher-dimensional wavefunctions

We want to preserve the basic feature that $|\Psi|^2$ gives us the probability density of the position of a particle. However that position is now a 3D vector $\mathbf{r} = [x, y, z]^T$. Same as here, we shall use **boldface** to distinguish vectors from scalars. To preserve the probability density interpretation, the wavefunction must now be a complex function in three-dimension, i.e. taking a vector-valued argument. As in the box around Eq. (1.27) we then have:

Probability density and normalisation in 3D Now $|\Psi(\mathbf{r}, t)|^2 \, dV$ shall be the probability at time t to find the particle in an infinitesimal cubic volume $dV = dx \, dy \, dz$ near 3D position $\mathbf{r} = [x, y, z]^T$. Hence the normalisation becomes

$$\int d^3\mathbf{r} \, |\Psi(\mathbf{r}, t)|^2 = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \, |\Psi(x, y, z, t)|^2 = 1. \tag{4.1}$$

Note: We can also use ket vectors to represent quantum states as before, with position space representation $\Psi(\mathbf{r}) = \langle \mathbf{r} \,|\, \Psi \rangle$. Here is one more advantage of the bra-ket notation: we do not have to worry about the number of dimensions initially. Pretty much all of week 6 and week 7 is unchanged, going from 1D to 3D.

Nextly

Operators in 3D Also the position and momentum operators now become vectors (vector operators)

$$\hat{\mathbf{r}} = \begin{bmatrix} \hat{x} \\ \hat{y} \\ \hat{z} \end{bmatrix}, \quad \hat{\mathbf{p}} = \begin{bmatrix} \hat{p}_x \\ \hat{p}_y \\ \hat{p}_z \end{bmatrix} = \begin{bmatrix} -i\hbar\frac{\partial}{\partial x} \\ -i\hbar\frac{\partial}{\partial y} \\ -i\hbar\frac{\partial}{\partial z} \end{bmatrix}. \tag{4.2}$$

- Since the operators are vectors, also expectation values of operators are vectors, e.g.

  $$\langle\hat{\mathbf{r}}\rangle = \langle\,\Psi\,|\hat{\mathbf{r}}|\,\Psi\,\rangle = \begin{bmatrix} \langle\,\Psi\,|\hat{x}|\,\Psi\,\rangle \\ \langle\,\Psi\,|\hat{y}|\,\Psi\,\rangle \\ \langle\,\Psi\,|\hat{z}|\,\Psi\,\rangle \end{bmatrix} = \begin{bmatrix} \int d^3\mathbf{r}\;\Psi^*(\mathbf{r})x\Psi(\mathbf{r}) \\ \int d^3\mathbf{r}\;\Psi^*(\mathbf{r})y\Psi(\mathbf{r}) \\ \int d^3\mathbf{r}\;\Psi^*(\mathbf{r})z\Psi(\mathbf{r}) \end{bmatrix}. \tag{4.3}$$

  Note, each integration still is a 3D integration!

- Since we now have multiple components of the position and momentum operators, we have to revisit their commutator (compare Eq. (2.46)). You can show that

  $$\left[\hat{r}_n, \hat{p}_m\right] = i\hbar\delta_{nm}, \tag{4.4}$$

  using the same techniques as in Eq. (2.47) (exercise). We have used $\hat{r}_n$ to label the three components of $\hat{\mathbf{r}}$ and $\hat{p}_m$ for those of $\hat{\mathbf{p}}$.

We similarly generalize the

Schrödinger equations in 3D, which are now

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right)\Psi(\mathbf{r},t), \quad \text{(TDSE)} \tag{4.5}$$

$$E_n\phi_n(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right)\phi_n(\mathbf{r}). \quad \text{(TISE)} \tag{4.6}$$

where we have used the

Laplacian operator:

$$\Delta = \boldsymbol{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{4.7}$$

4.1.1 Simple quantum systems in three dimensions

Most of what we discussed in section 2 straightforwardly generalizes to 3D, and we will now briefly mention how. However since not much new physics or techniques is added here, we shall be brief. You may notice that most books do not discuss this step at all, for the same reason.

Harmonic oscillator in 3D: In three dimensions, the harmonic oscillator potential is

$$V(\mathbf{r}) = \frac{1}{2}m\left(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2\right). \tag{4.8}$$

Note that this is of the separable form

$$V(\mathbf{r}) = V_x(x) + V_y(y) + V_z(z), \tag{4.9}$$

which is not true for all 3D potentials. However whenever the potential takes this form, it is easy to see that we can just reduce the solution of the 3D TISE (4.6) to three separate solutions of a 1D TISE (one for each dimension).

Using the argumentation around Eq. (1.57), you can see (exercise) that the 3D TISE:

$$E\phi(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right)\phi(\mathbf{r}), \tag{4.10}$$

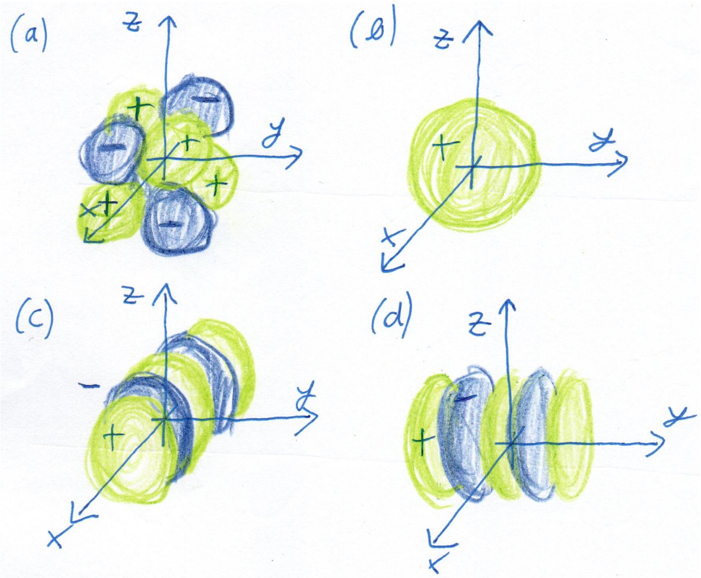
with $V(\mathbf{r})$ given by (4.8) and using the Ansatz $\phi(\mathbf{r}) = \varphi_{n_x}(x)\varphi_{n_y}(y)\varphi_{n_z}(z)$ is equivalent to three separate TISEs for each dimension:

$$\begin{aligned}
E_{n_x}\varphi_{n_x}(x) &= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_x(x)\right)\varphi_{n_x}(x),\\
E_{n_y}\varphi_{n_y}(y) &= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + V_y(y)\right)\varphi_{n_y}(y),\\
E_{n_z}\varphi_{n_z}(z) &= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + V_z(z)\right)\varphi_{n_z}(z). \qquad (4.11)
\end{aligned}$$

The total energy E in Eq. (4.10) is $E = E_{n_x} + E_{n_y} + E_{n_z}$, so that we should give the eigenvalue and eigenstate in Eq. (4.10) a vector subscript $\mathbf{n} = [n_x n_y n_z]$.

- Since each 1D equation in (4.11) takes the same form as (2.42), we immediately know the solution and energy eigenvalues.
- Note that for the approach it was crucial that we can write the potential as a sum of terms for each dimension, as in (4.8). Without that, the separation of variables near Eq. (1.57) would not work.

Example 28, Quantum states of the three-dimensional oscillator: A problem with 3D states is, that it becomes difficult to draw them



left: On the left we tried anyway, showing 3D equal-probability surfaces for selected states (a) $\mathbf{n} = [n_x = 1, n_y = 1, n_z = 1]$, (b) $\mathbf{n} = [000]$, (c) $\mathbf{n} = [400]$, b) $\mathbf{n} = [040]$ assuming $\omega_x = \omega_y = \omega_z = \omega$.

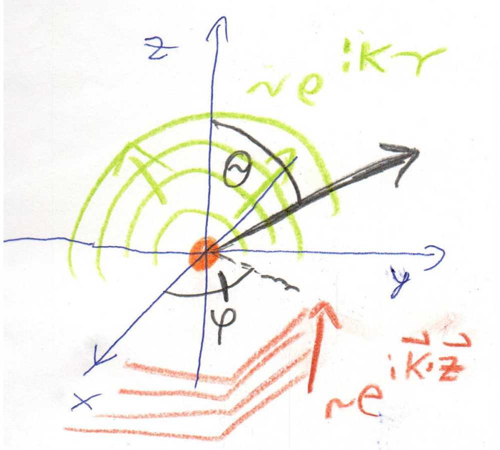
We see that "each dimension can be excited or not excited separately". A new feature emerging for the isotropic oscillator in 3D, is that all excited states are degenerate, since $E = \hbar\omega(n_x + n_y + n_z + \frac{3}{2})$. Hence e.g. $\mathbf{n} = [400]$ and $\mathbf{n} = [040]$ have the same energy. The physical difference between the states, is the <u>direction</u> along which the oscillator is moving.

Infinite square well potential: Consider the infinite square well in 3D, which is

$$\begin{aligned} V(\mathbf{r}) &= \infty, \qquad \text{if } x < 0,\ x > a,\ y < 0,\ y > a,\ z < 0,\ z > a, \\ V(\mathbf{r}) &= 0 \qquad \text{else.} \end{aligned} \tag{4.12}$$

We can again write this as a sum of a potential of the type (2.10) for each dimension separately, similar to (4.8). Hence also here the solution follows as a product $\phi(\mathbf{r}) = \varphi_{n_x}(x)\varphi_{n_y}(y)\varphi_{n_z}(z)$ of 1D solution and the energy as a sum $E = E_{n_x} + E_{n_y} + E_{n_z}$.

Scattering: We had seen a 1D scattering problem in section 2.2.3 for the example of the finite well. Here there were two possible outcomes: (i) transmission and (ii) reflection. In 3D, if an incoming, non-bound quantum particle impacts on a potential $V(\mathbf{r})$, there are of course many more outcomes:



left: The particle can afterwards be scattered into any direction $\mathbf{k}$ in 3D space, parametrised by two scattering angles as shown in the figure on the left.

It is the subject of quantum scattering theory, which we will learn in the next semester, to find out the probability for each direction.

Free particle and Gaussian wavepacket: Turning the free-particle Hamiltonian (2.1) into a 3D version we find

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta, \tag{4.13}$$

with Laplacian Δ from (4.7). From this we find the

Momentum eigenstates (3D) (plane wave solutions)

$$\phi(\mathbf{p},\mathbf{r}) = \frac{1}{\sqrt{2\pi\hbar}} e^{i\frac{\mathbf{p}}{\hbar}\cdot\mathbf{r}} \tag{4.14}$$

with $\hat{\mathbf{p}}\phi(\mathbf{p},\mathbf{r}) = \mathbf{p}\phi(\mathbf{p},\mathbf{r})$.

- Alternatively we can use the wave vector $\mathbf{k} = \frac{\mathbf{p}}{\hbar}$ in the notation above.
- These are now 3D plane waves, with propagation direction along $\mathbf{k}$.
- You can verify that these are eigenstates of (4.13) by simple differentiation.

Similarly we can generalize the

Gaussian Fourier transform pair (in 3D) Using $\sigma_k = 1/\sigma$, we have

$$\phi(\mathbf{r}) = \frac{1}{(\pi\sigma^2)^{3/4}} e^{-\frac{(\mathbf{r}-\mathbf{r}_0)^2}{2\sigma^2}} e^{i\mathbf{k}_0\cdot(\mathbf{r}-\mathbf{r}_0)}, \tag{4.15}$$

$$\tilde{\phi}(\mathbf{k}) = \frac{1}{(\pi\sigma_k^2)^{3/4}} e^{-\frac{(\mathbf{k}-\mathbf{k}_0)^2}{2\sigma_k^2}} e^{-i\mathbf{r}_0\cdot\mathbf{k}}. \tag{4.16}$$

- This is not the most general Gaussian, for that the widths in the three cartesian directions might differ $\sigma_x \neq \sigma_y \neq \sigma_z$

4.1.2 Angular momentum operator

In 3D we can meaningfully form one more operator our of the position and momentum ones, that did not make sense to define in 1D, the

Angular momentum operator

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}, \tag{4.17}$$

in the position representation $\hat{\mathbf{L}} = [\hat{L}_x, \hat{L}_y, \hat{L}_z]^T$, with

$$\begin{aligned} \hat{L}_x = \hat{L}_1 &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \\ \hat{L}_y = \hat{L}_2 &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \\ \hat{L}_z = \hat{L}_3 &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \end{aligned} \tag{4.18}$$

- This follows from the classical definition of angular momentum

  $$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{4.19}$$

  The angular momentum depends on the origin of your coordinate system (i.e. one should always say “ angular momentum with respect to ....”). Often (but not necessarily), angular momentum is used to characterise some sort of circular or orbital motion, such as a planet around the sun, or an electron around a proton.

When dealing with cross-products ×, it is often helpful to use the

Component notation for cross-product: For the cross-product $\mathbf{a} \times \mathbf{b} = \mathbf{c}$, we can write

$$c_i = \sum_{jk} \epsilon_{ijk} a_j b_k, \tag{4.20}$$

where ϵ_{ijk} is called Levi-Civita symbol or perfectly anti-symmetric tensor. Its indices i, j, k can take the values $1, 2, 3$ or x, y, z for the three dimensions of space, and $\epsilon_{123} = 1$. Whenever two indices are equal, it is zero, $\epsilon_{ijj} = 0$. Whenever you swap two indices, it changes sign, e.g. $\epsilon_{132} = -1$. A useful consequence is that the ϵ tensor remains constant under a cyclic change of indices, e.g. $1 = \epsilon_{123} = \epsilon_{231} = \epsilon_{312}$.
To use the Levi-Civita symbol, we often need the identity

$$\sum_i \epsilon_{ijk}\epsilon_{inm} = \delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km}. \tag{4.21}$$

With that we can write

$$\hat{L}_i = \sum_{jk} \epsilon_{ijk} \hat{x}_j \hat{p}_k. \tag{4.22}$$

Using the definitions (4.18) and the known commutators for position and momentum (4.4), you can (and should) show yourself the following commutator(s):

Commutator of angular momentum operator

$$\left[\hat{L}_n, \hat{L}_m\right] = i\hbar \sum_{\ell} \epsilon_{nm\ell} \hat{L}_\ell = i\hbar \epsilon_{nm\ell} \hat{L}_\ell. \tag{4.23}$$

- You can either use the explicit definitions (4.18) and show this three times (for $[nm\ell] = [xyz, yzx, zxy]$, or use the epsilon tensor notation (4.22) and the properties of ϵ plus (4.21) together with $\frac{\partial}{\partial_{x_k}} x_\ell = \delta_{k\ell}$ to show it only once.
- Since $\ell = 1, 2, 3$ and the epsilon tensor vanishes for two equal indices, we can write the RHS with or without the sum, usually it is written without.

Defining further the

Square of angular momentum

$$\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \tag{4.24}$$

we can show further that

$$\left[\hat{\mathbf{L}}^2, \hat{L}_n\right] = 0 \tag{4.25}$$

for any n. Let's see now what all these commutation relations tell us: We can immediately insert those into the generalized uncertainty principle (3.44), to see (exercise) the

Angular momentum uncertainty relation

$$\sigma_{L_x} \sigma_{L_y} \geq \frac{\hbar}{2} |\langle \hat{L}_z \rangle|. \tag{4.26}$$

similarly for $xyz \leftrightarrow yzx \leftrightarrow zyx$.

- We again see a deep difference to classical mechanics. In classical mechanics we can have a well defined position and momentum of the particle, and thus via (4.19) know all three components of the angular momentum perfectly.
- Quantum mechanically, (4.26) tells us that for non-zero angular momentum, you can know at most one component of the angular momentum vector perfectly.
- However, from using the generalized HUP with (4.25) we see that it IS possible to simultaneously have complete knowledge of the squared angular momentum $\hat{\mathbf{L}}^2$ and $\hat{L}_n$ for any one out of three cartesian components $n \in \{x, y, z\}$.

4.1.3 More particles

So far we considered the quantum mechanics of a single particle only. Of course most real world systems are made of many. We will start looking more seriously at that case in chapter 5, but we shall require the most basic statements regarding this already for our discussion of the Hydrogen atom (which is made of two particles, electron and proton, of course).

The first question is, what is the wavefunction of a two-particle system? For a single particle, $|\Psi(\mathbf{r},t)|^2\,dV$ is the probability at time t to find the particle within volume dV near $\mathbf{r} = [x, y, z]^T$. For two particles, we now have two 3D coordinates $\mathbf{r}_a$ and $\mathbf{r}_b$. Whenever either of these differs, the two-particle configuration has changed. The generalisation of our earlier single particle treatment is thus to use the

Two particle wavefunction

$$\Psi(\mathbf{r}_a, \mathbf{r}_b, t) \tag{4.27}$$

that has now one 3D coordinate $\mathbf{r}_k$ for each particle $k \in \{a, b\}$. We now say that the probability at time t to find particle a within volume dV near $\mathbf{r}_a = [x_a, y_a, z_a]^T$ and particle b within volume dV near $\mathbf{r}_b = [x_b, y_b, z_b]^T$ is $|\Psi(\mathbf{r}_a, \mathbf{r}_b, t)|^2\,dV^2$.

- Similarly the Hamiltonian now must contain kinetic energy and potential energy contributions for each particle. Stick with the example of two (non-interacting) particles:

$$\hat{H} = -\frac{\hbar^2}{2m_a}\Delta_{\mathbf{r}_a} - \frac{\hbar^2}{2m_b}\Delta_{\mathbf{r}_b} + V(\mathbf{r}_a) + V(\mathbf{r}_b), \tag{4.28}$$

  where $\Delta_{\mathbf{r}_a}$ denotes the Laplacian wrt. the components in vector $\mathbf{r}_a$ only.

- You hopefully see, that this gets nasty really fast, once we are looking at genuinely many particles. Even the wavefunction for just 10 particles is a 30 dimensional function.

Example 29, Many-body quantum problem: Assume we try to handle N distinguishable particles in 3D on a computer as we did in assignment 2,3. For that we now have to discretise each dimension of the wavefunction. Let's suppose we choose M discrete points for each, where typically $M \geq 64$ say, to get reasonable results. A typical floating point complex number takes 16 bytes of memory. How much memory do we need to store the 3D wavefunction of just $N = 3$ particles with $M = 64$ gridpoints per dimension?

Week ⑨

PHY 303 Quantum Mechanics
Instructor: Sebastian Wüster, IISER Bhopal, 2023

These notes are provided for the students of the class above only. There is no guarantee for correctness, please contact me if you spot a mistake.

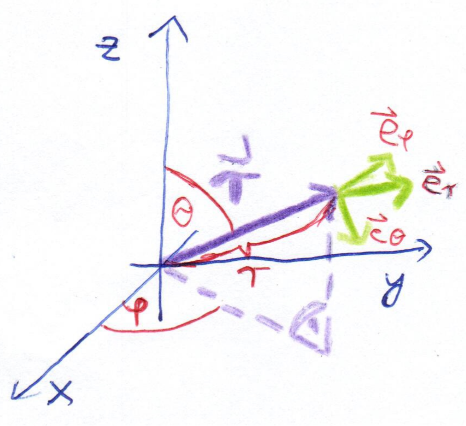
4.2 Spherically symmetric potentials

The 3D potentials we had discussed in the previous week were all such that the problem is separable, due to (4.9). In that case the TISE can frequently be solved analytically even if the potential is not symmetric (such as (4.8) with the $\omega_k \neq \omega_\ell$ for $k \neq \ell$). We shall now look at cases that are not easily separable, but in which the potential is spherically symmetric:

$$V(\mathbf{r}) = V_r(r), \tag{4.29}$$

with $r = \sqrt{x^2 + y^2 + z^2}$. We have used the radial coordinate from

Spherical polar coordinates:



left: We express our position vector as

$$\mathbf{r} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} r\sin\theta\cos\varphi \\ r\sin\theta\sin\varphi \\ r\cos\theta \end{bmatrix} \tag{4.30}$$

in terms of a radius $r = |\mathbf{r}| = \sqrt{x^2 + y^2 + z^2}$, a polar angle (co-latidude) θ and an azimuthal angle (longitude) φ, as sketched on the left. We can find the latter two from the cartesian coordinates via $\theta = \arccos(z/r)$ and $\varphi = \text{atan2}(y, x)$. The latter is $\arctan(y/x)$ for $x, y > 0$.

We also have to change our set of unit vectors, from the cartesian ones $\mathbf{e}_x = [1, 0, 0]^T$, $\mathbf{e}_y = [0, 1, 0]^T$, $\mathbf{e}_z = [0, 0, 1]^T$ to spherical polar unit vectors (green in the figure).

$$\mathbf{e}_r = \begin{bmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{bmatrix}, \quad \mathbf{e}_\theta = \begin{bmatrix} \cos\theta\cos\varphi \\ \cos\theta\sin\varphi \\ -\sin\theta \end{bmatrix}, \quad \mathbf{e}_\varphi = \begin{bmatrix} -\sin\varphi \\ \cos\varphi \\ 0 \end{bmatrix}. \tag{4.31}$$

Note that $\mathbf{e}_r = \frac{\partial}{\partial r}\mathbf{r}$, $\mathbf{e}_\theta = \frac{\partial}{\partial \theta}\mathbf{e}_r$ and $\mathbf{e}_\varphi \parallel \frac{\partial}{\partial \varphi}\mathbf{e}_r$.

For setting up the coordinates above, we can for the moment freely chose what we call the z-axis. We shall get back to this subtle point at the end of week 10.

Example 30, Coulomb potential: The obvious example for a spherically symmetric potential is the Coulomb potential V_{coul} felt by a particle of charge q near another one of charge Q, where we place the latter at the origin:

$$V_{\text{coul}}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0}\frac{qQ}{r} = \frac{1}{4\pi\epsilon_0}\frac{qQ}{\sqrt{x^2+y^2+z^2}}, \tag{4.32}$$

where ϵ_0 is the vacuum permittivity. We have written the potential in spherical polar coordinates and cartesian coordinates, to highlight how much simpler it looks in polar ones, and how it can not be separated in the form (4.9) using cartesian coordinates.

Due to the simplicity of a spherically symmetric potential in spherical polar coordinates, we want to rewrite the TISE (4.6) for those cases entirely in those coordinates. The main challenge is to change the Laplacian, which is a nasty technical operation, the result of which we take from mathematics courses:

Laplacian in spherical polar coordinates:

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}. \tag{4.33}$$

Inserting this into (4.6), for a particle of mass m, we now want to solve the time-independent

Schrödinger equation for spherically symmetric potentials

$$\begin{aligned} &-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\phi_n(r,\theta,\varphi) \\ &+ V(r)\phi_n(r,\theta,\varphi) = E_n\phi_n(r,\theta,\varphi). \end{aligned} \tag{4.34}$$

In order to get this tidied up a bit, we can be guided by our knowledge of classical mechanics: We know, for example from the treatment of the Kepler problem, that for a spherically symmetric potential (central force), angular momentum is conserved. This motivates us to attempt to re-express parts of (4.34) using the angular momentum operator (4.17). To do that, we first express it also in spherical polar coordinates. This is easy for the position operator, which just becomes $\hat{\mathbf{r}} = \hat{r}\mathbf{e}_r$. For the momentum operator we need the

Three dimensional gradient: in spherical polar coordinates

$$\boldsymbol{\nabla} = \mathbf{e}_r\frac{\partial}{\partial r} + \mathbf{e}_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + \mathbf{e}_\varphi\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi} \tag{4.35}$$

with unit vectors defined in (4.31).

Inserting this for the momentum operator in (4.17) you can convince yourself (exercise/Griffith) that we get the following

Position space representation of the angular momentum operator For the operator itself, we find

$$\hat{\mathbf{L}} = -i\hbar \left(\mathbf{e}_\varphi \frac{\partial}{\partial\theta} - \mathbf{e}_\theta \frac{1}{\sin\theta}\frac{\partial}{\partial\varphi} \right) \tag{4.36}$$

and for the angular momentum square consequently

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \right) \tag{4.37}$$

Note, that to get from (4.36) to (4.37) you need to be careful that derivatives in the left operator of $\hat{\mathbf{L}}^2 = \mathbf{L}\cdot\mathbf{L}$ act on angles within the unit vectors (4.31) of the right one.
Finally using $\hat{L}_z = \mathbf{e}_z \cdot \hat{\mathbf{L}}$, Eq. (4.36) and Eq. (4.31) we have

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}, \tag{4.38}$$

for the z-component of angular momentum.

Comparing (4.37) with (4.34) we spot, that we can write the latter (somewhat more tidily) as:

$$\underbrace{\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{\mathbf{L}}^2}{2mr^2} + V(r) \right]}_{=\hat{H}} \phi_n(r,\theta,\varphi) = E_n\phi_n(r,\theta,\varphi). \tag{4.39}$$

- You can easily show that $\left[\hat{H},\hat{L}\right] = 0$. According to Eq. (3.54), this means that angular momentum is conserved, as we know it has to be in a central potential.
- According to section 3.8, in quantum mechanics this implies that we can expect the eigenfunctions of the Hamiltonian to simultaneously be eigenfunctions of the angular momentum operator, as we indeed will see shortly.
- Conservation of angular momentum is deeply connected to the spherical symmetry, or in other words rotational invariance of the central force problem. You have learnt (or will learn) in classical mechanics, that for a continuous rotational symmetry Noether's theorem enforces angular momentum to be conserved. Similarly in quantum mechanics, we could show directly from the the rotational symmetry of the Hamiltonian, that angular momentum must be conserved (see Griffith chapter 6 for further reading).

Since only $\hat{L}$ contains derivatives with respect to angles, we can hope to sort r and angles θ, φ apart, and again use our separation of variables trick from section 1.6.5. We make the Ansatz

$$\phi(r,\theta,\varphi) = R(r)Y(\theta,\varphi), \tag{4.40}$$

suppressing the index n. Inserting this into (4.39), we then bring everything with r onto the LHS of the resultant equation, and everything with θ and φ onto the RHS, concluding that both sides have to be equal to the same constant C (exercise, see Griffith), which we call $C = \ell(\ell+1)$ for reasons that shall become clear later.

After separation of variables, we reached a

Separated Schrödinger equation in a central potential. For 3D wavefunction (4.40), the radial part $R(r)$ fulfills the radial Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right)+\underbrace{\left[V(r)+\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]}_{\equiv V_{\text{eff}}(r)}R(r)=ER(r) \tag{4.41}$$

and the angular part $Y(\theta,\varphi)$ fulfills the angular Schrödinger equation

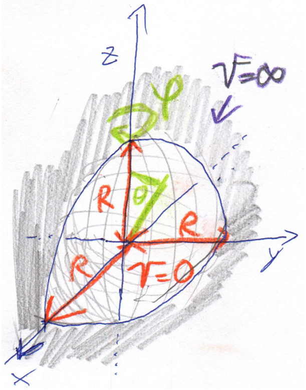
$$-\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)Y(\theta,\varphi)=\hat{\mathbf{L}}^2Y(\theta,\varphi)=\hbar^2\ell(\ell+1)Y(\theta,\varphi). \tag{4.42}$$

- We see from the second equality in (4.42) that the angular equation tells us that the angular part $Y(\theta,\varphi)$ of the 3D wavefunction is an eigenfunction of the square of angular momentum, with eigenvalue $\hbar^2\ell(\ell+1)$.
- The radial equation (4.41) looks like[13] a 1D Schrödinger equation with an effective potential $V_{\text{eff}}(r)$. Since we can see from (4.42) without having solved anything that $\hbar^2\ell(\ell+1)$ will be the eigenvalue of the angular momentum squared, we recognize this effective potential as exactly the same one that you have encountered in the classical mechanics of the central force problem. We thus interpret that extra part $\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$ as centrifugal potential.
- The splitting into Eq. (4.41) and Eq. (4.42), can always be done in the form above, independent of the detailed form of $V(r)$ as long as $V(\mathbf{r})$ depends only on the radius $r=|\mathbf{r}|$. We thus see that for this important class of problems, eigenfunctions of the square of the angular momentum operator play a special role. We will thus have to look at these more closely in the next section.

---

[13] The derivative term is slightly off from our 1D TISE, but that can be cured with a simple substitution (see Griffith or section 4.6 here later).

Example 31, Infinite spherical well: A simple extension of our earlier topic in section 2.2.1 would be to consider the infinite spherical well in three dimensions.



left: We (badly) tried to sketch this on the left. The potential is $V(\mathbf{r}) = 0$ within some radius R, where $r = |\mathbf{r}| < R$, and $V(\mathbf{r}) = \infty$ outside.

The discussion so far applies to this potential, so that we can separately deal with the angular part of the wavefunction (exactly as in the following section), and the radial part (see Griffith if you are interested).

4.3 Angular momentum eigenfunctions

To find all solutions of the angular equation (4.42) (divided by $-\hbar^2$), we can make use of separation of variables one final time. We make the Ansatz

$$Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi), \tag{4.43}$$

and again (successfully, exercise, Griffith) separate all dependence on θ onto the LHS and all dependence on φ onto the RHS. The two separated equations that we find are:

$$\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right)\right] = (m^2 - \ell(\ell+1)\sin^2\theta)\Theta(\theta), \tag{4.44}$$

$$\frac{d^2}{d\varphi^2}\Phi(\varphi) = -m^2\Phi(\varphi) \tag{4.45}$$

This time we have called the separation constant m^2. At this point we do not yet know what m will be, but it has nothing to do with the particle mass. We call it m because everybody does, and you shall see later that there is no real danger of confusion.

To know more about m: The second equation (4.45) is easy to solve and gives us

$$\Phi(\varphi) = e^{im\varphi}. \tag{4.46}$$

From our coordinate definition (4.30) we see that the azimuthal angle φ and $\varphi + 2\pi$ correspond to the same point. For a reasonable wavefunction, we this need $\Phi(\varphi) = \Phi(\varphi + 2\pi)$, which you can reform into $e^{2\pi i m} = 1$, giving us $m = 0, \pm 1, \pm 2, \pm 3$ etc, i.e. m must be an integer. We have thus again found a quantisation rule, even though at this point we are not sure yet what is being quantised (but we shall see that shortly).

The first equation (4.44) is evidently somewhat more complicated. We take its direct solution from the mathematical physics literature for now, and I will show you a tricky way of finding the answer in the next section 4.4. It turns out (4.45) is solved by $\Theta(\theta) = \mathcal{N} P_\ell^m(\cos\theta)$, where $\mathcal{N}$ is a normalisation factor and we used the

Associated Legendre function: defined by

$$P_\ell^m(x) = (1-x^2)^{|m|/2} \left(\frac{d}{dx}\right)^{|m|} P_\ell(x). \tag{4.47}$$

As seen above, these are in turn obtained via differentiation from P_ℓ, the ℓ'th Legendre polynomial

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \left(\frac{d}{dx}\right)^{\ell} (x^2-1)^\ell, \tag{4.48}$$

defined for $\ell \geq 0$.

- As the name suggests, the Legendre polynomial P_ℓ is a polynomial of degree ℓ, you can find a few explicit examples in Griffith. I will wait with examples until we have the complete $Y(\theta,\varphi)$ shortly.
- Since Legendre polynomials P_ℓ are of degree ℓ, we see that associated Legendre functions $P_\ell^m(x)$ for $|m| > \ell$ do not exist (or are zero). We thus only need to consider $|m| \leq \ell$.
- Recall that we are on the way of solving the 3D TISE for a wavefunction Ansatz $\phi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$. For a normalized wavefunction, we require

  $$1 = \int d^3\mathbf{r}\, |\phi(r,\theta,\varphi)|^2 = \int_0^\infty dr\, r^2 |R(r)|^2 \underbrace{\int d\Omega}_{\equiv \int_0^\pi d\theta \sin(\theta) \int_0^{2\pi} d\varphi} |Y(\theta,\varphi)|^2, \tag{4.49}$$

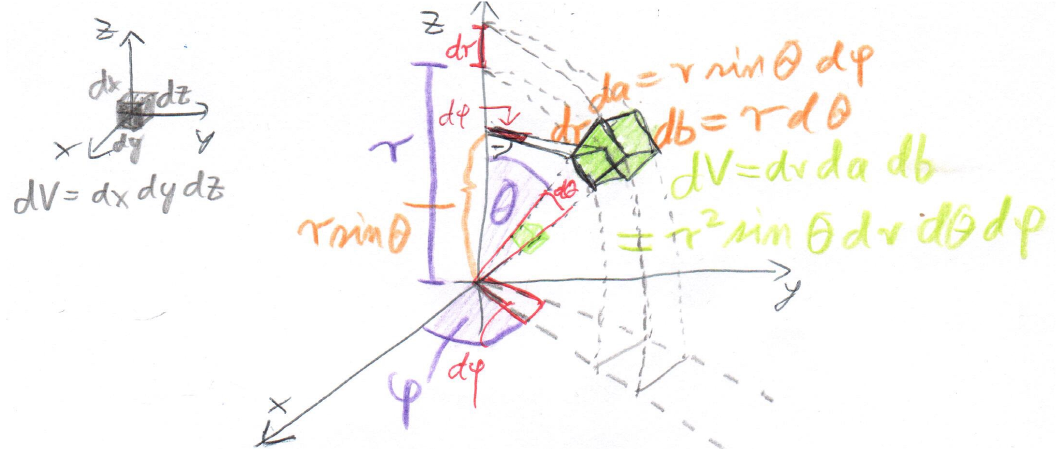
  where we have defined the integration $\int d\Omega$ over the 3D solid angle. (If you are not familiar with 3D integrations in spherical polar coordinates, refer to the yellow box below) From the above expression it is clear that it is practical to separately normalize $\int_0^\infty dr\, r^2 |R(r)|^2 = 1$ and

  $$\int_0^\pi d\theta \sin(\theta) \int_0^{2\pi} d\varphi |Y(\theta,\varphi)|^2 = 1, \tag{4.50}$$

  which we can use to fix the constant $\mathcal{N}$ in $\Theta(\theta)$ above.

Integration in spherical polar coordinates:

In the same way that a 1D integration $I = \int dx f(x)$ is ultimately defined as $I = \lim_{dx\to 0}\sum_k dx f(x_k)$ where dx is an infinitesimal length near x along the x axis, we can define the 3D one as $I = \lim_{dV\to 0}\sum_k dV f(\mathbf{r}_k)$, where dV is an infinitesimal volume around $\mathbf{r}$. In cartesian coordinates we can easily write $dV = dxdydz$, see figure below.



top: Infinitesimal volume element dV in cartesian coordinates (left) and in polar coordinates (right). There is a **mistake** at the orange brace that says "$r\sin\theta$" this should be $r\cos\theta$ instead and the upper edge of that triangle is $r\sin\theta$, as required.
There is two ways to understand how to find $dV = r^2\sin\theta dr d\theta d\varphi$ in polar coordinates:

(i) Vector-calculus math courses will generalize the transformation $I = \int dx f(x) \to I\int du\frac{dx(u)}{du}f(u)$ to three dimensions. If we know (x, y, z) as a function of (r, θ, φ) and the reverse (this is called a variable transformation), mathematician will tell us that we have to multiply the Jacobian of the transformation J into the integral when converting, so that $dxdydz \to \underbrace{r^2\sin\theta}_{=J} dr d\theta d\varphi$.

(ii) If you want to understand more intuitively why this is the right expression, consider the above drawing of a spherical polar volume element and listen to the discussion of its geometry in the video.

Fixing the normalisation constant as discussed above, and putting it all together, we have now found the

Eigenfunction of the angular motion in a spherically symmetric potential are given by the spherical harmonics

$$Y_\ell^m(\theta,\varphi) = (-1)^m\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}e^{im\varphi}P_\ell^m(\cos\theta). \tag{4.51}$$

where the angular momentum quantum number $\ell = 0, 1, 2, 3, \cdots$ is an integer, as is the magnetic quantum number $|m| \le \ell$.

- We had started off by re-expressing parts of the Hamiltonian in (4.34) using the angular momentum operator, and then we were able to find the angular part of the 3D wavefunction (i.e. its θ and φ dependence) based entirely on the angular momentum operator. The angular part thus exclusively encodes the angular momentum properties of our particle in 3D. Directly from the original equation we already know that $Y_\ell^m(\theta,\varphi)$ is an eigenfunction of $\hat{\mathbf{L}}^2$ with eigenvalue $\hbar^2\ell(\ell+1)$, thus the magnitude of angular momentum is

$$|\hat{\mathbf{L}}| \equiv \hbar\sqrt{\ell(\ell+1)}. \tag{4.52}$$

- From Eq. (4.38) it is also easy to see that we have

  $$\hat{L}_z Y_\ell^m(\theta,\varphi) = (-i\hbar\frac{\partial}{\partial\varphi})Y_\ell^m(\theta,\varphi) = (\hbar m)Y_\ell^m(\theta,\varphi), \tag{4.53}$$

  which implies that the spherical harmonics are also eigenfunctions of the z-component of angular momentum, with eigenvalue $\hbar m$.

- Having a fixed value for $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ is the maximum amount of information we can have about the angular momentum, as we have seen in section 4.1.2 (please revisit that now): Since $\left[\hat{L}_n, \hat{L}_m\right] = i\sum_\ell \epsilon_{nm\ell}\hat{L}_\ell$ (Eq. (4.23)), we can know at most one component of the vector without uncertainty. However since $\left[\hat{\mathbf{L}}^2, \hat{L}_n\right] = 0$, we are allowed to additionally know $\hat{\mathbf{L}}^2$.

- With the prefactors given in Eq. (4.51), the spherical harmonics are normalized when integrated over the solid angle of all space, see Eq. (4.50):

  $$\int d\Omega |Y_\ell^m(\theta,\varphi)|^2 = \int_0^\pi d\theta \sin(\theta) \int_0^{2\pi} d\varphi |Y_\ell^m(\theta,\varphi)|^2 = 1. \tag{4.54}$$

- As all eigenfunctions of a Hermitian operator, they are mutually orthogonal:

  $$\int d\Omega \ \left[Y_{\ell'}^{m'}(\theta,\varphi)\right]^* Y_\ell^m(\theta,\varphi) = \int_0^\pi d\theta \sin(\theta) \int_0^{2\pi} d\varphi \ \left[Y_{\ell'}^{m'}(\theta,\varphi)\right]^* Y_\ell^m(\theta,\varphi) = \delta_{\ell\ell'}\delta_{mm'}. \tag{4.55}$$

  Note that here the $*$ is really crucial, since the spherical harmonics are usually complex (unless $m=0$).

- Like with all eigenfunctions, the $Y_\ell^m(\theta,\varphi)$ are only specified up to a complex phase (in particular up to a factor (-1)), by the equations that define them. For that reason there are unfortunately different sign conventions used in different contexts. Whenever practically making use of them, one thus have to be careful. We gave the sign convention usually used in quantum mechanics for physicists. Already chemists might use different ones. They even might like real spherical harmonics.

- The application of spherical Harmonics is much wider than in quantum mechanics: They are a useful tool whenever one has to expand a function f defined on the surface of a sphere via angles θ and φ:

  $$f(\theta,\varphi) = \sum_{\ell,m} c_{\ell,m} Y_\ell^m(\theta,\varphi). \tag{4.56}$$

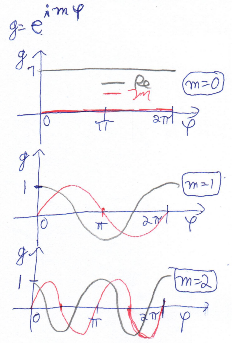
  This surface could be the surface of the earth, or the sky as seen from earth or a spherical object in engineering. Roughly speaking coefficients $c_{0,0}$ with $\ell=0$ then provide the part of that function that does not vary with angles, while coefficients $c_{\ell,m}$ with higher ℓ and m, the more rapid the variations of that function with angle.

	$m=0$	$m=\pm1$	$m=\pm2$
$\ell=0$	$Y_{00}=\frac{1}{\sqrt{4\pi}}$		
$\ell=1$	$Y_{10}=\sqrt{\frac{3}{4\pi}}\cos\theta$	$Y_{1\pm1}=\mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\varphi}$	
$\ell=2$	$Y_{20}=\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$	$Y_{2\pm1}=\mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\varphi}$	$Y_{2\pm2}=\mp\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm2i\varphi}$
$\ell=3$	$Y_{30}=\sqrt{\frac{7}{16\pi}}(5\cos^3\theta-\cos\theta)$	$Y_{3\pm1}=\mp\sqrt{\frac{21}{64\pi}}\sin\theta(5\cos^2\theta-1)e^{\pm i\varphi}$	$Y_{3\pm2}=\sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta e^{\pm2i\varphi}$
	$m=\pm3$		
	$Y_{3\pm3}=\mp\sqrt{\frac{35}{64\pi}}\sin^3\theta e^{\pm3i\varphi}$		

Table 2: List of the lowest few spherical harmonics $Y_\ell^m(\theta,\varphi)$ from (4.51).

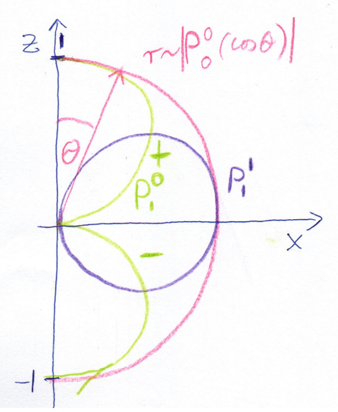
We list the first few spherical harmonics in table 2, you can easily find more in other sources.

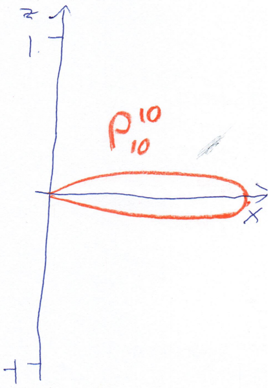
Example 32, Sketches of spherical harmonics: In addition to table 2 it is useful to visualize the angular momentum eigenfunctions:



left: The part related to the quantum number m and hence the z-component of the angular momentum is easy to draw, see left. If we compare this with our 1D plane waves e^{ikx} from section 2.1, we realize this corresponds to angular motion with "wavenumber" $k_\varphi = m$.

The polar part dependent on θ is more difficult to draw. Me made a "polar graph" below.

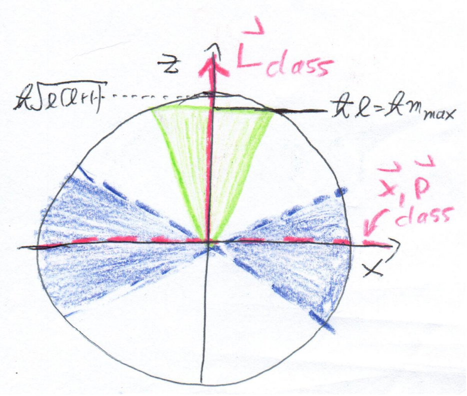




left: You have to select an angle θ from the origin, then the distance of the line from the origin is given by $|P_\ell^m(\cos\theta)|$ and the sign is additionally indicated. We can see that for larger ℓ the function changes more rapidly along θ, while m additionally decides in which direction(s) the function is nonzero.

One example that we can understand based on our understanding of classical mechanics is $P_\ell^{m=\ell}$ for large ℓ, e.g. $\ell = 10$. This amounts to a large angular momentum, oriented strongly along the z-axis. Hence motion is mainly (but not quite perfectly) in the $x-y$ plane, see also next example.

Example 33, Angular momentum uncertainty cones:



left: The maximum allowed value of m is $m = \ell$. For that case, if we compare the eigenvalue of $|\hat{\mathbf{L}}|$ which is $\hbar\sqrt{\ell(\ell+1)}$, with that of $\hat{L}_z$ which is $\hbar\ell$, we see that $L_z < |L|$, never quite being equal. This means that for large ℓ the state $m = \ell$ corresponds to the angular momentum pointing almost entirely but not quite along the z-axis. We know from Eq. (4.23) that it cannot point with certainty along the z-axis, since then we would know $L_x = L_y = 0$.

Instead the latter must have some residual uncertainty, which is encoded in the angular momentum lying within the green cone (think of it rotated around the z-axis to form a cone. Classically we know the motion must be in a plane perpendicular to the angular momentum (violet lines). Applied to the uncertainty cone, it must then lie in the blue shaded region (again think 3D, rotated around z)

Most of the above will become clearer when we combine it with the radial wavefunction in the case of Hydrogen, so if you were confused, wait until section 4.6.2 and then refer to the above again.

4.4 Algebraic treatment of angular momentum

Similarly to the harmonic oscillator in section 2.3, we can find the eigenvalue structure of angular momentum entirely without reference to position space wavefunctions, based on commutator algebra and the commutation relation (4.23).

We again start by the definitions of

Ladder operators for angular momentum

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y. \tag{4.57}$$

Using the basic rules for commutators (3.45), you can show as an easy exercise that

$$\left[\hat{L}_z, \hat{L}_\pm\right] = \pm\hbar\hat{L}_\pm, \tag{4.58}$$

$$\left[\hat{\mathbf{L}}^2, \hat{L}_\pm\right] = 0. \tag{4.59}$$

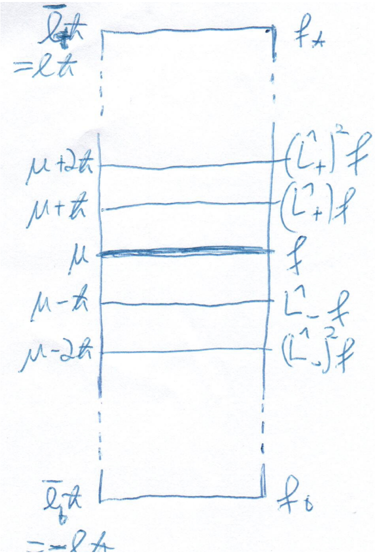
Now the argumentation proceeds very similar to the one for the harmonic oscillator. Let us assume that f was an eigenfunction of the square of angular momentum $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ with "some" (unknown) eigenvalue for either, hence $\hat{L}_z f = \mu f$ and $\hat{\mathbf{L}}^2 f = \lambda f$. Then

$$\hat{L}_z(\hat{L}_\pm f) = \hat{L}_z\hat{L}_\pm f \underbrace{-\hat{L}_\pm\hat{L}_z f + \hat{L}_\pm\hat{L}_z f}_{=0} = \underbrace{\left[\hat{L}_z, \hat{L}_\pm\right]}_{\overset{Eq.\ (4.58)}{=} \pm\hbar\hat{L}_\pm} f + \hat{L}_\pm \underbrace{\hat{L}_z f}_{=\mu f} = (\mu \pm \hbar)\hat{L}_\pm f. \tag{4.60}$$

We have thus shown, that if the function f has the eigenvalue μ wrt $\hat{L}_z$, then the function $\hat{L}_\pm f$ has the eigenvalue $\mu \pm \hbar$. Similarly

$$\hat{\mathbf{L}}^2(\hat{L}_\pm f) \overset{Eq.\ (4.59)}{=} \hat{L}_\pm \underbrace{\hat{\mathbf{L}}^2 f}_{=\lambda f} = \lambda \hat{L}_\pm f, \tag{4.61}$$

which means that $\hat{L}_\pm f$ remains an eigenfunction of $\hat{\mathbf{L}}^2$ with the same eigenvalue λ that f had.



left: In conclusion, similar to ladder operators for the harmonic oscillator, the ones for angular momentum are climbing up and down "a ladder" of different eigenvalues for $\hat{L}_z$, without changing those of $\hat{\mathbf{L}}^2$, as sketched on the left.
As with the oscillator this cannot go on arbitrarily. It should be intuitive that we require $\langle \hat{L}_z^2 \rangle \leq \langle \hat{\mathbf{L}}^2 \rangle$ (we can proof this, but it is a bit tricky). Hence there shall again be a top and bottom rung of the ladder, such that $\hat{L}_+ f_t = 0$ and $\hat{L}_- f_b = 0$. We expect the maximum and minimal value of $m\hbar$ to be somehow related to ℓ.

To find out how exactly they are related, let us look at $\hat{\mathbf{L}}^2 f_t$. In preparation, we can show (Griffith/exercise), that

$$\hat{\mathbf{L}}^2 = \hat{L}_\pm \hat{L}_\mp + \hat{L}_z^2 \mp \hbar \hat{L}_z. \tag{4.62}$$

Applying the lower sign of Eq. (4.62) to the top state (top rung of the ladder) gives

$$\hat{\mathbf{L}}^2 f_t = \hat{L}_- \underbrace{\hat{L}_+ f_t}_{=0} + \underbrace{\hat{L}_z^2 f_t}_{=(\hbar\bar{\ell}_t)^2 f_t} + \hbar \underbrace{\hat{L}_z f_t}_{=\hbar\bar{\ell}_t f_t} = \hbar^2 \bar{\ell}_t(\bar{\ell}_t + 1) f_t. \tag{4.63}$$

Similarly, using (4.62) with the upper sign and applying it to the bottom state (bottom rung of the ladder)

$$\hat{\mathbf{L}}^2 f_b = \hat{L}_+ \underbrace{\hat{L}_- f_b}_{=0} + \underbrace{\hat{L}_z^2 f_b}_{=(\hbar\bar{\ell}_b)^2 f_b} - \hbar \underbrace{\hat{L}_z f_b}_{=\hbar\bar{\ell}_b f_b} = \hbar^2 \bar{\ell}_b(\bar{\ell}_b - 1) f_b. \tag{4.64}$$

At the same time, we already know from before that $\hat{\mathbf{L}}^2 f_t = \lambda f_t = \hbar^2 \ell(\ell+1) f_t$ and $\hat{\mathbf{L}}^2 f_b = \lambda f_b = \hbar^2 \ell(\ell+1) f_b$ with <u>the same</u> ℓ, which is the orbital quantum number. We thus have the two equations

$$\ell(\ell+1) = \bar{\ell}_t(\bar{\ell}_t + 1), \qquad \ell(\ell+1) = \bar{\ell}_b(\bar{\ell}_b - 1), \tag{4.65}$$

which come up with four solutions for $\bar{\ell}_t$ and $\bar{\ell}_b$. Out of those only one has the required property that $\bar{\ell}_t > \bar{\ell}_b$ and that is $\bar{\ell}_t = \ell$ and $\bar{\ell}_b = -\ell$. Since we are reaching from $-\ell$ to ℓ in N integer steps, we must have $\ell = N/2$, so ℓ must be an <u>integer or half-integer</u>. The case of integers reproduces the ranges for the azimuthal quantum number m that we had listed near Eq. (4.51). The possibility of half-integer ℓ will be used for spin in section 4.7.1.

4.5 Position representation of angular momentum states

To use the algebraic treatment to also find the position space states in section 4.3, we again mirror what we did for the harmonic oscillator. First we require the

Position space representation of ladder operators

$$\hat{L}_{\pm} = \pm\hbar e^{\pm i\varphi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\varphi}\right). \tag{4.66}$$

- You can show this using Eq. (4.36) and Eq. (4.57).

We now know that $\hat{L}_+ Y_\ell^\ell = 0$, which using (4.66) becomes

$$\hbar e^{\pm i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right) Y_\ell^\ell(\theta,\varphi) = 0. \tag{4.67}$$

We already know from (4.46) that the φ dependence takes the form $e^{im\varphi}$, which we can use here: Because of it we know that $\frac{\partial}{\partial\varphi} Y_\ell^\ell(\theta,\varphi) = i\ell Y_\ell^\ell(\theta,\varphi)$. Inserting that gives

$$\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)\underbrace{Y_\ell^\ell(\theta,\varphi)}_{=e^{i\ell\varphi}\Theta_\ell^\ell(\theta)} = 0 \Leftrightarrow \left(\frac{\partial}{\partial\theta} - \ell\cot\theta\right)\Theta_\ell^\ell(\theta) = 0 \tag{4.68}$$

Using $d\sin\theta/d\theta = \cos\theta$ and $\cot\theta = \cos\theta/\sin\theta$, we can reshape this as

$$\begin{aligned} \frac{d\Theta_\ell^\ell(\theta)}{\Theta_\ell^\ell(\theta)} &= \ell\frac{d(\sin\theta)}{\sin\theta}, \Leftrightarrow \\ \log\Theta_\ell^\ell(\theta) &= \ell\log(\sin\theta) + const, \quad \Leftrightarrow \quad \Theta_\ell^\ell(\theta) = \mathcal{N}(\sin\theta)^\ell. \end{aligned} \tag{4.69}$$

where $\mathcal{N}$ can be fixed by normalisation. We can now find all the other angular momentum eigenfunctions down to $Y_\ell^{-\ell}$ by repeatedly applying $\hat{L}_-$ as in (4.66). What we find, up to a sign, is (4.51). Unfortunately that is not quite obvious, but if you are sceptical about the statement you can try it out at least for the few examples given in table 2.

We have now worked out all important properties of the eigenfunction of the angular momentum operators $\hat{\mathbf{L}}^2$ and $\hat{L}_z$. These functions describe the angular part of quantum states and quantum dynamics whenever the potential is spherically symmetric. In the next week we finally also sort out the radial part, for which we have to pick a specific potential. We shall of course pick the one for the Hydrogen atom.

Week ⑩

PHY 303 Quantum Mechanics
Instructor: Sebastian Wüster, IISER Bhopal, 2023

The angular momentum eigenfunctions for the part describing the coordinates θ and φ in spherical polar coordinates that we discussed so far are valid for an arbitrary spherically symmetric potential, and besides the symmetry do not depend on the detailed form $V(r)$ of that potential. What remains to be done to find all 3D solutions of the TISE is to specify a radial potential $V(r)$ and then solve the radial Schrödinger equation (4.41).

4.6 Hydrogen atom

We shall do this now for the specific example of the Hydrogen atom. However, recall that our entire discussion so far was for a single particle, while a Hydrogen atom consists of two particles, the electron and the proton.

4.6.1 Separation of centre-of-mass motion [Bonus]

Luckily the problem simplifies to an effective single particle problem. The reasoning is the same as in classical mechanics, hence I shall not repeat it here fully, but instead refer you to the solution of the Kepler planetary problem in classical mechanics PHY305. Note that the coulomb potential and the gravitational potential have the exact same mathematical form, depending like $1/|\mathbf{r}_1 - \mathbf{r}_2|$ on the separation between the two bodies. Let the proton be at $\mathbf{r}_p$ with mass M_p and the electron at $\mathbf{r}_e$ with mass m_e. We then define the centre of mass coordinate $\mathbf{R}$, the relative coordinate $\mathbf{r}$ the total mass M and the reduced mass μ though the relations:

$$\begin{aligned} M = m_e + M_p, \qquad \mu = \frac{m_e M_p}{m_e + M_p}, \\ \mathbf{R} = \frac{M_p \mathbf{r}_p + m_e \mathbf{r}_e}{M}, \qquad \mathbf{r} = \mathbf{r}_e - \mathbf{r}_p. \end{aligned} \tag{4.70}$$

Note, that since $M_p \approx 2000 m_e$, we have $\mathbf{R} \approx \mathbf{r}_p$, $M \approx M_p$ and $\mu \approx m_e$.

The Hamiltonian (operator) for a proton and electron starts off as (see e.g. (4.28))

$$\hat{H} = -\frac{\hbar^2}{2m_p}\Delta_{\mathbf{r}_p} - \frac{\hbar^2}{2m_e}\Delta_{\mathbf{r}_e} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_e - \mathbf{r}_p|}. \tag{4.71}$$

It turns out that using the definitions (4.70), we can transform (4.71) into a Hamiltonian expressed in terms of centre of mass and relative coordinates.

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2M}\Delta_{\mathbf{R}}}_{\hat{H}_{CM}} \underbrace{-\frac{\hbar^2}{2\mu}\Delta_{\mathbf{r}} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}|}}_{=\hat{H}_{rel}} . \tag{4.72}$$

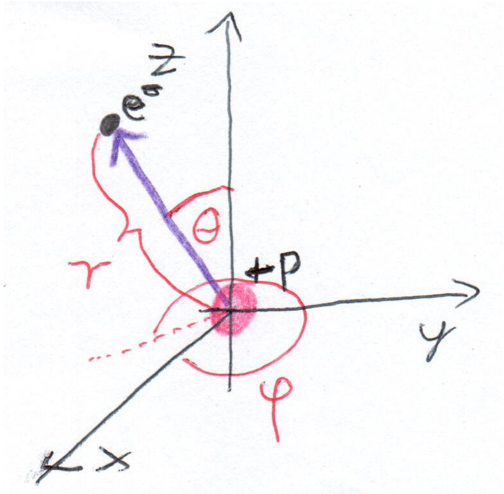
As we had seen in section 4.1.3, for the two-particles, the wavefunction now becomes six-dimensional: $\phi_{p+e}(\mathbf{R}, \mathbf{r})$. As we had seen in section 4.1.1, whenever the Hamiltonian is a sum of Hamiltonians for the two different coordinates, as is the case in (4.72), we can write the wavefunction as a product

$$\phi_{p+e}(\mathbf{R}, \mathbf{r}) = \phi_{CM}(\mathbf{R})\phi_{rel}(\mathbf{r}). \tag{4.73}$$

and then do a separation of variables (see section 1.6.5) to split the TISE or TDSE following from (4.72) into two separated ones for the centre-of-mass wavefunction $\phi_{CM}(\mathbf{R})$ and the relative wavefunction $\phi_{rel}(\mathbf{r})$. The centre-of-mass wavefunction $\phi_{CM}(\mathbf{R})$ will just behave like that for a free particle as discussed in section 2.4. The relative wavefunction is affected by the Coulomb potential as evident from (4.72) and thus will describe binding of the electron to the proton.

In the following we shall just assume that the proton is infinitely heavy, so that $\mu \to m_e$, and we work in the centre of mass frame (proton frame) of the atom. Then also the problem reduces to a single particle problem, that of the electron, using only $\phi_{rel}(\mathbf{r})$. However bear in mind, that to be precise, in all what follows we have to replace the mass of the electron m_e with the reduced mass of the electron-proton system μ.

4.6.2 Hydrogen wavefunctions



left: Assuming an infinitely heavy proton as discussed in the previous section, we use spherical polar coordinates to describe the location of the electron, with the proton at the origin of the coordinate system. The situation is sketched once more on the left, but really this is just the same diagram as that in section 4.2.

We know the electron mass is $m_e = 9.109 \times 10^{-31}$ kg, and the potential with which it interacts with the proton is the Coulomb potential (4.32), where $q = -e$ is the electron charge and $Q = +1$ that of the proton, while r is the distance between them. The potential in this section is thus

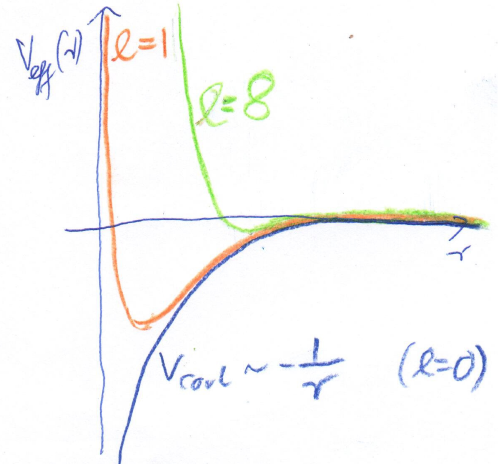
$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}. \tag{4.74}$$

The situation clearly is spherically symmetric, so that that our discussion of section 4.2 so far fully applies. This means that 2/3 of the work are already done. We can write the 3D wavefunction of the electron as in Eq. (4.40):

$$\phi(r,\theta,\varphi) = R(r)Y(\theta,\varphi), \tag{4.75}$$

and already know the possible forms of Y depending on the angular momentum of the electron. What remains to be done is to solve the radial SE (4.41) to find $R(r)$. It turns out we can make the equation slightly simpler by the substitution $u(r) = rR(r)$, then, also using Eq. (4.74)

$$-\frac{\hbar^2}{2m_e}\frac{d^2}{dr^2}u(r) + \underbrace{\left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}\right]}_{\equiv V_{\text{eff}}(r)} u(r) = Eu(r). \tag{4.76}$$



left: We are showing a drawing of the effective potential $V_{\text{eff}}(r)$ for a few values of ℓ on the left. Clearly, depending on the quantum number ℓ for the magnitude of angular momentum, see Eq. (4.52), there is an increasing centrifugal potential that pushes the electron outwards. This is what you also encountered in the solution of the Kepler problem of a planet orbiting the sun, only there classically. In contrast to classical mechanics, the centrifugal potential can only take certain shapes since angular momentum is quantised.

As we had seen in the case of the finite potential well in section 2.2.2, the TISE here admits two kinds of solutions, scattering states with $E > 0$ and bound states with $E < 0$. The former would describe the situation where an electron comes in with a positive energy from infinity, makes a fly-by past the proton (i.e. "scatters from it") and then again escapes with conserved energy to infinity. In contrast, of course, in the bound state the electron is "stuck to the proton". We will only consider bound states here, hence $E < 0$.

To solve (4.76), we proceed with the same recipe as in section 2.3.2. We first make the equation dimensionless, to reduce the clutter in the notation. This is done by the redefinition $\rho = \kappa r$ with $\kappa = \sqrt{-2mE}/\hbar > 0 \in \mathbb{R}$ and the shorthand $\rho_0 = \frac{m_e e^2}{2\pi\epsilon_0\hbar^2\kappa}$ for which Griffith gives a bit of a motivation. We reach

$$\frac{d^2u(\rho)}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u(\rho). \tag{4.77}$$

As in section 2.3.2 we try to first understand the asymptotic behaviour of $u(\rho)$. For $\rho \to \infty$, the only term in $[\cdots]$ that remains is the 1, so we have $\frac{d^2u(\rho)}{d\rho^2} = u(\rho)$, with the general solution $u(\rho) = Ae^{-\rho} + Be^{\rho}$. Clearly the second term would not be normalizable, so we settle with $u(\rho) = Ae^{-\rho}$ for large ρ (and large ρ implies large r).

At small $\rho \to 0$, the centrifugal term $\sim \ell$ in $[\cdots]$ dominates, hence $\frac{d^2u(\rho)}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u(\rho)$, with general solution $u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}$ (check by back-substitution). But the second term blows up at $\rho \to 0$ so we set $D = 0$.

Most of the arguments above are not super rigorous (e.g. not valid for all values of ℓ), but they only serve to motivate one further re-definition of the function that we are solving for:

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho). \tag{4.78}$$

(we could have done even without any of the arguments above). Inserting (4.78) into (4.77) we reach

$$\rho \frac{d^2 v(\rho)}{d\rho^2} + 2(\ell + 1 - \rho) \frac{dv(\rho)}{d\rho} + [\rho_0 - 2(\ell+1)] v(\rho) = 0. \tag{4.79}$$

Finally, again as in section 2.3.2 we take a power series Ansatz for $v(\rho)$

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j, \tag{4.80}$$

plug that into (4.79) and obtain a recursion relation for the coefficients:

$$a_{j+1} = \frac{2(j + \ell + 1) - \rho_0}{(j+1)(j + 2\ell + 2)} a_j. \tag{4.81}$$

Of course we could have done the power series Ansatz for $u(\rho)$ directly and plugged that one into (4.77), but it turns out that that would be much more messy (see Griffith's footnote on page 136). We can again see that if the series would not terminate, the resultant function $u(\rho)$ would not be normalisable according to Eq. (4.49) (see technical arguments in Griffith). The termination must happen as in section 2.3.2, we require a maximum power j, let's say $j_{\max}$, for which the numerator of the fraction in (4.81) vanishes, such that $a_{j_{\max}+1}$ and all subsequent coefficients vanish. Hence

$$2(j_{\max} + \ell + 1) - \rho_0 = 0 \tag{4.82}$$

Let us define a new integer

$$n = j_{\max} + \ell + 1 \tag{4.83}$$

such that (4.84) becomes $2n = \rho_0$ and using the definition of ρ_0, which contains the energy, we can finally write this termination condition as:

$$E = E_n = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2}. \tag{4.84}$$

Since n is an integer, we thus found a quantized energy yet again. Also note, that since $j_{\max} \geq 0$ we automatically have $n \geq \ell + 1$ or the other way round $\ell \leq n - 1$. It remains to find the wavefunction, for which we have to solve the recursion relation (4.81) for finding $v(\rho)$. Due to the termination condition (4.84) and (4.80) we already know that $v(\rho)$ is a polynomial of degree $j_{\max} = n - \ell - 1$. Mathematicians finally tell us that it is $v(\rho) = L^{2\ell+1}_{n-\ell-1}(2\rho)$ in terms of the

Associated Laguerre polynomial: which is derived via

$$L^p_{q-p}(x) = (-1)^p \left(\frac{d}{dx} \right)^p L_q(x) \tag{4.85}$$

from the q'th Laguerre polynomial:

$$L_q(x) = e^x \left(\frac{d}{dx} \right)^q (e^{-x} x^q). \tag{4.86}$$

For our later drawings of Hydrogen wavefunctions, we need the first few associated Laguerre polynomials:

$$L_0^0 = 1, \quad L_1^0 = -x + 1, \quad L_2^0 = x^2 - 4x + 2, \quad L_1^0 = 1, \quad L_1^1 = 1 - 2x + 4, \quad L_2^1 = 3x^2 - 18x + 18. \tag{4.87}$$

More of them can be found in Griffith or the internet.

Due to the form $v(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho)$, we see that the wavefunction depends on n and ℓ, as we would have expected since the differential equation (4.76) contains E (related to n through (4.84)) and separately also ℓ. Undoing all our substitutions further above, adding the angular momentum part, and inserting quantum numbers, we have found the wavefunction

$$\begin{aligned} \phi_{n\ell m}(r,\theta,\varphi) &= R_{n\ell}(r) Y_\ell^m(\theta,\varphi), \\ R_{n\ell}(r) &= \frac{1}{r}\rho^{\ell+1} e^{-\rho} v_{n\ell}(\rho), \end{aligned} \tag{4.88}$$

with dimensionless coordinate $\rho = r/(a_0 n)$, where we used the

Bohr radius

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 5.29 \times 10^{-11}\text{m}. \tag{4.89}$$

We have purposefully waited for the red boxes until now, to collect the complete

Electronic states and energies of the Hydrogen atom The energy of the electron in the Hydrogen atom is

$$E_n = -\underbrace{\frac{m_e e^4}{8\epsilon_0^2 h^2}}_{=R^*}\frac{1}{n^2}. \tag{4.90}$$

where the Rydberg energy is $R^* = 13.6$ eV.
The corresponding complete and normalised wavefunctions are

$$\phi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r) Y_\ell^m(\theta,\varphi), \tag{4.91}$$

$$R_{n\ell}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!]}} e^{-r/(na_0)} \left(\frac{2r}{na_0}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right), \tag{4.92}$$

with spherical harmonics $Y_\ell^m(\theta,\varphi)$ given in (4.51).

- The hydrogen states depend on three quantum-numbers n, ℓ and m.
  - The principal quantum number[14] n is the only one that affects the energy of the electron, it describes the quantisation of energy. Its range is $n = 1, 2, \cdots$ the positive integers.

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[14] Not principlE quantum number

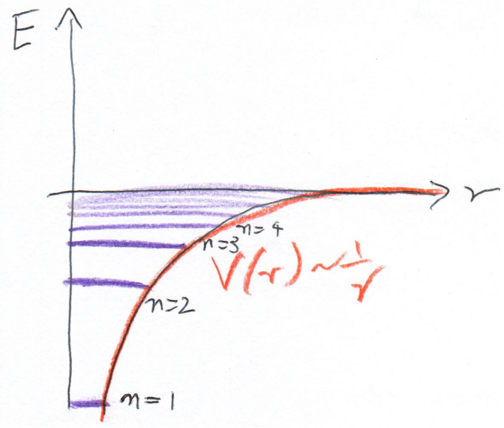
There is no maximal value. We can infer this range from the definition (4.83), with $j_{\max}, \ell \geq 0$ (see below). This quantum number affects the <u>radial part</u> $R_{n\ell}(r)$ of the wavefunction in (4.91), but not the angular one $Y_\ell^m(\theta, \varphi)$.

  - The <u>orbital quantum number</u> ℓ describes the <u>quantisation of the magnitude of (orbital) angular momentum</u>, as seen in (4.52). It is the only quantum number that affects <u>both parts</u> of the wavefunction, the radial one and the angular one. It can take the values $0 \leq \ell \leq n-1$. That ℓ is a positive integer we had seen in section 4.3, while the requirement $\ell \leq n-1$ again follows from (4.83).
  - The <u>magnetic quantum number</u> m describes the <u>quantisation of the z-component of (orbital) angular momentum</u>, as seen in (4.53). It is an integer that can take the range $-\ell \leq m \leq +\ell$, as we had seen in section 4.3.

- For many, the Hydrogen atom will remain the most complex quantum problem for which you will see a complete analytical solution. That solution however is extremely important. With some slight modifications for larger atoms (PHY 402) it underpins our understanding of the periodic table, the existence of spectral lines (PHY 106) and atom-light interaction. With the latter, we can engineer many important tools for modern quantum experiments and technologies.

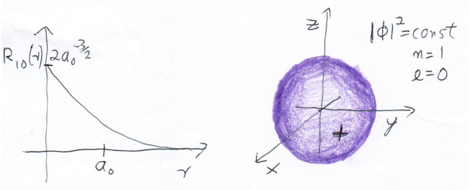
- A historic artefact that has remained useful due to avoiding cluttering notation with too many numbers is the <u>spectroscopic notation</u>, where we replace the orbital quantum number with a letter code $\ell = 0, 1, 2, 3, 4, \cdots \rightarrow s, p, d, f, g, \cdots$ (at $\cdots$ it continues alphabetically). We can then write e.g. the state with quantum numbers $n = 2$ and $\ell = 1$ as $|\, 2p\, \rangle$ and so forth. In PHY402 you shall see an extension of this notation that includes also the total angular momentum including spin, and its orientation.

Due to this widespread importance, and the lack of examples in section 4.2 let's see a few more examples and drawings here:



left: First let's sketch the Hydrogen energies as we did earlier inside of a drawing of the Coulomb potential $V(r)$ ((4.74)). Energy levels are not equidistant, with energy gaps decreasing between adjacent states of higher principal quantum number n. The classical turning point where $E = V(r)$ is moving further and further out. Mathematically, there is an infinite number of states as we approach $E \rightarrow 0$ from below. Practically, at some point these electrons are so weakly bound that such states would not be very relevant, except in outer space or very well shielded experiments.

Example 34, Lower quantum states of Hydrogen: Now let's revisit drawings of Hydrogen wavefunctions that we already saw in PHY106, but where now we know the (almost) complete derivation:



left: The simplest but also most important is the Hydrogen ground state $|\,1s\,\rangle$ (hence $n=1$, which forces $\ell=0$ and hence $m=0$). We draw the radial wavefunction

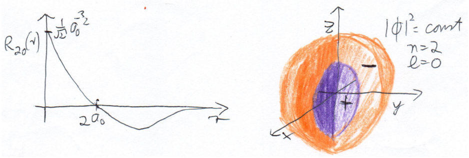
$$R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0} \tag{4.93}$$

on the left, it drops exponentially, with length-scale (=size of the atom), given by the Bohr radius a_0.

In the right panel above, we draw an "equal probability surface" in 3D, e.g. the sphere where $|\phi(\mathbf{r})| = const$. It is a sphere, because

$$Y_{00}(\theta,\varphi) = \frac{1}{\sqrt{4\pi}} \tag{4.94}$$

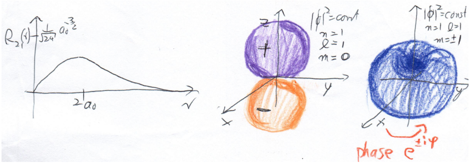
is spherically symmetric (since it simply does not depend on any angle).



left: The first excited state $n=2$ allows several different angular momentum states. For $|\,2s\,\rangle$, i.e. $n=2$, $\ell=0$, $m=0$, we again have a spherical symmetry using (4.94), but now we have one node in the radial wavefunction, see Eq. (4.87):

$$R_{20}(r) = \frac{1}{2\sqrt{6}a_0^{3/2}}\left(1-\frac{r}{2a_0}\right)e^{-r/(2a_0)} \tag{4.95}$$

The drawing is supposed to show a sphere, out of which we have cut out a quadrant to look inside and show the sign.



left: When angular momentum is nonzero $\ell=1$, it can point in three different directions $m=+1,0,-1$. Independent of that, the radial wave function looks as on the left,

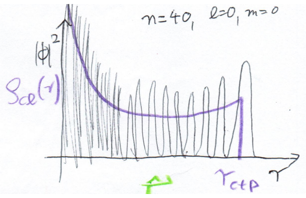
$$R_{21}(r) = \frac{1}{2\sqrt{6}a_0^{3/2}}\frac{r}{a_0}e^{-r/(2a_0)} \tag{4.96}$$

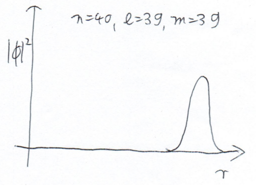
with reduced probability density at the proton. This is a consequence of the centrifugal barrier in V_{eff}, see Eq. (4.41).

The angular wavefunctions are now no longer spherically symmetric, with

$$Y_{10}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta, \qquad Y_{1\pm1}(\theta,\varphi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\varphi}. \tag{4.97}$$

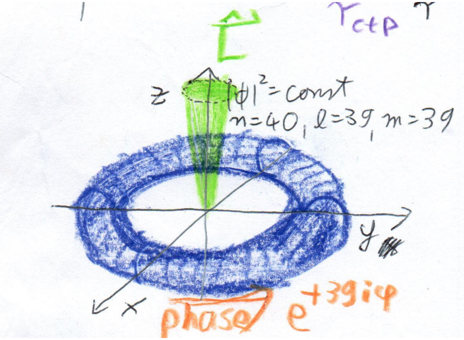
Example 35, Rydberg states of Hydrogen: We had seen many examples before, where low energy quantum states do not seem to have much in common with our classical physics intuition, but high lying ones do, see e.g. example 15. This is also the case for the Hydrogen atom, hence we take a look at its Rydberg states, which means large n (say $n > 10$).





left: Due to the structure of the Laguerre polynomials, the radial wave- function of Hydrogen has $j = n - \ell = 1$ nodes. For $n = 40$ and $\ell = 0$ the gives a highly oscillatory probability density as shown on the left.

If we smoothen the fast oscillations, we obtain a probability density that resembles that of a classical electron in a Coulomb potential $\rho_{cl}(r)$, shown in violet. As usual, the quantum results reaches farther than the classical turning point r_{ctp}, there showing exponential decay.
In contrast, for the maximum possible $\ell = 39$, there are no nodes and the radial wavefunction appears almost Gaussian, centered on large radii.



left: If we look into the 3D probability density we see why: This forms a torus/donut as shown left. Together with the radial phase $e^{39i\varphi}$ this implies the electron making an almost "circular orbit" around the proton, like a planet.

The angular momentum implied by this state is also shown in green. We see that the motion is almost constrained to a the $x - y$ plane, as it would be classically, also revisit example 33.

4.6.3 Meaning of the z-axis

Now that we are done with the Hydrogen atom, we should wonder about what is special about the z-axis[15]. The answer is of course "nothing", the Coulomb potential (4.74) is perfectly symmetric. However changing the z-axis does change the meaning of all our Hydrogen eigenstates states $\phi_{n\ell m}(\mathbf{r})$ as you can see from e.g. the drawing in example 35: For the state shown, if we chose a different z-axis, we get a completely different torus orientation. How can this be reconciled?

Degeneracy of angular momentum states. We see in Eq. (4.90) that energy only depends on n. We see in (4.52) that the magnitude of angular momentum only depends on ℓ. Together this means that all states with different azimuthal quantum numbers m are degenerate in both, energy and magnitude of angular momentum. As written in the (newly added, please read now) section 3.4.1, whenever that is the case we have some freedom to chose our eigen-basis within the

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[15] In fact we should wonder that already at the end of week 9.

degenerate subspace. For the case here, that means that any function

$$\tilde{Y}_\ell^m(\theta,\varphi) = \sum_{m'} c_{m'}^{(\ell\, m)} Y_\ell^{m'}(\theta,\varphi), \tag{4.98}$$

will also be an eigenfunction of the Hamiltonian and the magnitude of angular momentum (but no longer of the z-component of the angular momentum). With this construction, it it possible to "rotate" the orbital shapes in example 34 into different "directions", see video. This is done for example in the real spherical harmonics used in chemistry. So also the mathematics reproduces the features that the z-axis can be chosen arbitrarily.

Degeneracy of angular momentum states. In practice though, there typically is a smart choice of z-axis and lots of bad choices. This is because (except in this course), we never consider the Hydrogen atom in isolation. You are either concerned with its excitation by light or its interrogation by light. Usually this means that calculations get easier, if you choose your z-axis along a physically meaningful direction, e.g. that of the polarisation of the electric field in the light. Nevertheless, you are free to chose any other axis, at the expense of "requiring more states" in your calculation.

Week ⑪

PHY 303 Quantum Mechanics
Instructor: Sebastian Wüster, IISER Bhopal, 2023

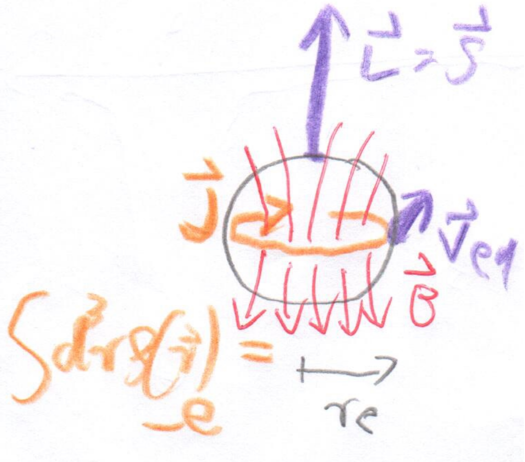
These notes are provided for the students of the class above only. There is no guarantee for correctness, please contact me if you spot a mistake.

4.7 Spin

The angular momentum that we have discussed in section 4.1.2 and section 4.3 was orbital angular momentum. It arises through motion of a particle in space relative to a point, such as the electron orbiting the proton, see section 4.6. It turns out that there is also another type of angular momentum in nature, which is intrinsic to fundamental particles (and hence not related to any spatial motion as per present understanding). This is called spin, essentially for historic reasons and for an intuitive but wrong (see example 37) picture of it involving the fundamental particle spinning about its body axis.

Example 36, Experimental requirement for spin: We had learnt in PHY106 that the lines in Hydrogen spectra are due to photons of frequency ω carrying the energy that matches the difference $\hbar\omega_{nm} = (E_n - E_m)$ between two energy levels as in Eq. (4.90). It turns out that Eq. (4.90) only describes experimental observations correctly when looking on large energy scales. When zooming in onto a given spectral lines, these typically split up into multiple lines even for an isolated atom. This is called e.g. fine-structure (PHY304/402) and is not described by Eq. (4.90). One also observes that lines split into more lines when the atom is placed into a magnetic field. This is called Zeeman effect (PHY304/402). Again the splittings can usually not be explained by the states $\phi_{n\ell m}$ in Eq. (4.91). So what is going on?

Example 37, Electron as a spinning charged sphere (classical picture): Goudsmit and Uhlenbeck proposed that the electron carries an intrinsic angular momentum and magnetic moment.



left: Both could be the case if the electron was e.g. a uniformly charged sphere that is spinning about its own axis, as shown on the left. The circulating charge represents a current loop as shown, which creates a magnetic field using the right hand rule.

Example continued: You can calculate using PHY305 that the angular momentum of a sphere of mass m_e and radius r_e spinning with angular frequency ω is $S = I\omega$, with moment of inertia $I = \frac{2}{5} m_e r_e^2$. Experiments deduced that the intrinsic angular momentum of the electron has magnitude $S = \hbar\sqrt{s(s+1)}$ (compare Eq. (4.52)) with $s = \frac{1}{2}$, i.e. $S = \sqrt{3}\hbar/2$. Using $v_{eq} = \omega r_e$, with equatorial velocity v_{eq}, we find

$$v_{eq} = \frac{5\sqrt{3}}{4} \frac{\hbar}{m_e r_e}. \tag{4.99}$$

Inserting $m_e = 9.109 \times 10^{-31}$ kg and the present upper limit on the electron radius $r_e \approx 10^{-22}$ m (https://en.wikipedia.org/wiki/Electron), we find $v_{eq} \approx 8 \times 10^9 c$, for speed of light c. Clearly that cannot be right.

- The value given above is the present upper limit on r_e, however the theory presently takes the electron as a point-particle. Instead of the picture above, we thus accept the experimental evidence that it carries an intrinsic angular momentum (spin) of fixed magnitude $s = 1/2$ which we call $\hat{\mathbf{S}}$. Associated with that is an intrinsic magnetic moment $\hat{\mu} = -g\mu_B \hat{\mathbf{S}}$, where $\mu_B = e\hbar/(2m_e) = 9.27 \times 10^{-24}\ J/T$ is called the Bohr magneton, and $g \approx 2$ is called the electron g-factor.
- We know that the intrinsic quantity must be an angular momentum, because it behaves in every way like one, e.g. in conservation of angular momentum during photon emission of an atom.
- Some of you might learn later, in courses on relativistic quantum mechanics or quantum-field theory, that in order to construct a relativistic (that means Lorentz invariant) quantum theory of a charged particle like the electron, it needs to have a spin degree of freedom (its wavefunction must be a vector, not a scalar, see section 4.7.2).

4.7.1 Spin operators and states

Since we know that spin behaves just like an angular momentum, we can apply most of what we learnt earlier about orbital angular momentum (henceforth we call a non-spin angular momentum such as $\hat{\mathbf{L}}$ "orbital angular momentum", to emphasize the difference). We define the

Spin operator

$$\hat{\mathbf{S}} = [\hat{S}_x, \hat{S}_y, \hat{S}_z]^T, \tag{4.100}$$

and assume that the components of this vector operator fulfill the usual commutation relations for angular momentum, as in Eq. (4.23):

$$\left[\hat{S}_n, \hat{S}_m\right] = i\hbar \sum_{\ell} \epsilon_{nm\ell} \hat{S}_\ell. \tag{4.101}$$

In exact analogy to orbital angular momentum, we then also have additional

Spin commutation relations

$$\begin{aligned}
\left[\hat{S}_n, \hat{S}_m\right] &= i\hbar \sum_{\ell} \epsilon_{nm\ell} \hat{S}_\ell, \\
\left[\hat{\mathbf{S}}^2, \hat{S}_m\right] &= 0, \\
\left[\hat{S}_z, \hat{S}_\pm\right] &= \pm\hbar \hat{S}_\pm, \\
\left[\hat{\mathbf{S}}^2, \hat{S}_\pm\right] &= 0,
\end{aligned} \tag{4.102}$$

where we have used the spin ladder operators

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y, \tag{4.103}$$

again completely analogous to Eq. (4.57).

Since the algebraic construction of angular momentum states of section 4.4 was solely based on the angular momentum commutators, it fully applies here too. We just will replace $\ell \to s$ and $m \to m_s$, to indicate that we are dealing with spin. We also can never write a position space representation for spin states, so what earlier was $Y_\ell^m(\theta, \varphi)$ becomes $|\, s\, m_s \,\rangle$ now when dealing with spin. Hence we have the following

Spin quantum states $|\, s\, m_s \,\rangle$ (and their properties)

$$\hat{\mathbf{S}}^2 |\, s\, m_s \,\rangle = \hbar^2 s(s+1) |\, s\, m_s \,\rangle, \tag{4.104}$$

$$\hat{S}_z |\, s\, m_s \,\rangle = \hbar m_s |\, s\, m_s \,\rangle, \tag{4.105}$$

$$\hat{S}_\pm |\, s\, m_s \,\rangle = \hbar \sqrt{s(s+1) - m_s(m_s \pm 1)}\, |\, s\, (m_s \pm 1) \,\rangle, \tag{4.106}$$

with ranges $s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$ and $-s \le m_s \le s$ in integer steps.

- Recall that the discussion in section 4.4 gave us that m_s (earlier m) must range from some $-s$ to s (earlier ℓ) in integer steps. This is only possible if ℓ itself is an integer or half-integer. Hence the spin-quantum number s can take the values listed above.
- In contrast, for orbital angular momentum half-integer ℓ are excluded because these also give rise to half-integer values of m and then the $e^{im\varphi}$ part of the position representation of the angular wavefunction would not be single valued. For spin that constraint does not arise, since there is no *spatial* wavefunction associated with spin.
- It turns out that fundamental particles of a certain kind always carry a fixed value of the spin (electrons $s = 1/2$, photons $s = 1$ (with $m_s = 0$ forbidden), quarks $s = 1/2$).

4.7.2 Spin 1/2

The list above already shows why $s = 1/2$ is the most important (and luckily simplest) case. In that case there are only two possible m_s states which we write as $|\, s = \frac{1}{2},\ m_s = \pm\frac{1}{2}\,\rangle$ or shorter $|\,\frac{1}{2},\ \pm\frac{1}{2}\,\rangle$ or even shorter $|\uparrow\rangle = |\,\frac{1}{2},\ +\frac{1}{2}\,\rangle$ (called "spin-up") and $|\downarrow\rangle = |\,\frac{1}{2},\ -\frac{1}{2}\,\rangle$ (called "spin-down"). The Hilbertspace (see section 1.5.4) of (only the) spin of a spin-1/2 particle is thus two dimensional, spanned by the two basis states $|\uparrow\rangle$ and $|\downarrow\rangle$. This makes it particularly convenient to handle everything using matrix-representations (see section 3.3), for both, operators and states.

Since our vector space is just 2D, we can use basis vectors

$$\boldsymbol{\chi}_\uparrow = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \boldsymbol{\chi}_\downarrow = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{4.107}$$

The most general quantum state for a spin-1/2 is

$$|\,\Psi\,\rangle = c_\uparrow|\uparrow\rangle + c_\downarrow|\downarrow\rangle \tag{4.108}$$

with $|c_\uparrow|^2 + |c_\downarrow|^2 = 1$. In the matrix representation we can write this as

$$\boldsymbol{\chi} = \begin{bmatrix} c_\uparrow \\ c_\downarrow \end{bmatrix} = c_\uparrow\boldsymbol{\chi}_\uparrow + c_\downarrow\boldsymbol{\chi}_\downarrow. \tag{4.109}$$

This representation of the spin wavefunction is called a spinor.

We can invert the relations (4.106) to find

$$\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-), \qquad \hat{S}_y = \frac{1}{2i}(\hat{S}_+ - \hat{S}_-), \tag{4.110}$$

and then evaluate all possible matrix elements $\langle\, sm_s\,|\hat{O}|\,sm_{s'}\,\rangle$ for $s = 1/2$ and $m_s, m_{s'} \in \{1/2, -1/2\}$ for all spin operators $\hat{O}$ of interest, as we have done below. (There is only four matrix elements to evaluate for each).

Matrix representation of spin-operators

$$\underline{\underline{S_x}} = \frac{\hbar}{2}\underline{\underline{\sigma_x}}, \quad \underline{\underline{S_y}} = \frac{\hbar}{2}\underline{\underline{\sigma_y}}, \quad \underline{\underline{S_z}} = \frac{\hbar}{2}\underline{\underline{\sigma_z}}, \quad \underline{\underline{S_+}} = \hbar\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, \quad \underline{\underline{S_-}} = \hbar\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \tag{4.111}$$

where we have used the Pauli matrices

$$\underline{\underline{\sigma_x}} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \underline{\underline{\sigma_y}} = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \underline{\underline{\sigma_z}} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{4.112}$$

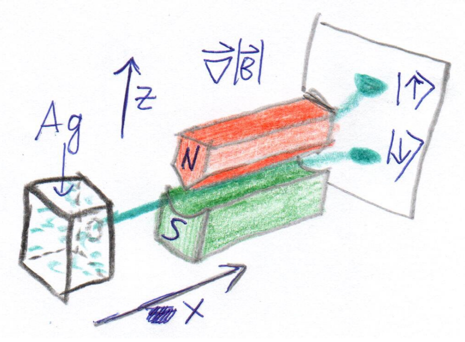
- The matrices for spin components are Hermitian as they should be, while those for ladder operator are not.
- The Pauli matrices together with the unit matrix $\mathbb{1}$ form a basis of the space of 2 × 2 Hermitian matrices. This means we can write the matrix representation of every operator for an observable in a 2D Hilbertspace as a sum of these matrices (operators), see also section 4.7.4: $\underline{\underline{O}} = c_1\mathbb{1} + c_x\underline{\underline{\sigma}}_x + c_y\underline{\underline{\sigma}}_y + c_z\underline{\underline{\sigma}}_z$, with real c_k.
- The eigenstates of $\hat{S}_z$ are $|\uparrow\rangle$ and $|\downarrow\rangle$ by definition.
- The matrix representations above make it easy to also find the eigenvectors for the other components, e.g. $\hat{S}_x$. In terms of eigenvectors of the matrix, these are

$$\boldsymbol{\chi}_{\leftarrow} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}, \quad \boldsymbol{\chi}_{\rightarrow} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}. \tag{4.113}$$

with $\underline{\underline{S_x}}\boldsymbol{\chi}_{\leftarrow} = +\frac{\hbar}{2}\boldsymbol{\chi}_{\leftarrow}$ and $\underline{\underline{S_x}}\boldsymbol{\chi}_{\rightarrow} = -\frac{\hbar}{2}\boldsymbol{\chi}_{\rightarrow}$. Converted again into bra-ket notation, this means

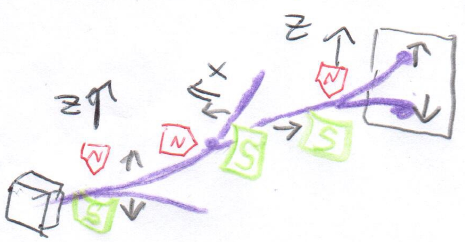
$$|\leftarrow\rangle = (|\uparrow\rangle + |\downarrow\rangle)/\sqrt{2}, \quad |\rightarrow\rangle = (|\uparrow\rangle - |\downarrow\rangle)/\sqrt{2}. \tag{4.114}$$

Example 38, Stern-Gerlach experiment: undertaken in 1922 to explore the quantization of angular momentum, see figure below. The Ag atom angular momentum is just given by the valence electron spin, since the net spin and orbital angular momentum of all other electrons happens to be zero. The atom thus has $s = 1/2$. The magnetic moment of the atom due to the electron is $\hat{\boldsymbol{\mu}} = -g_s\mu_B\hat{\mathbf{S}}/\hbar$, in an inhomogeneous magnetic field this yields a Force $\hat{\mathbf{F}} = -\boldsymbol{\nabla}[-\hat{\boldsymbol{\mu}}\cdot\mathbf{B}]$. With magnetic field and inhomogeneity along z we reach, all up: $F_z = -g_s\mu_B\hat{S}_z\frac{\partial}{\partial z}B_z$.



left: A beam of silver atoms is directed through a region of inhomogeneous magnetic field. The resultant different forces experienced by $|\uparrow\rangle$ and $|\downarrow\rangle$ atoms split the beam up into only two discrete spots. The device has thus demonstrated quantisation of $\hat{S}_z$ *and* measured the value of $\hat{S}_z$ for each atom (depending on whether it ended up in the top spot or bottom spot).

Example 39, Repeated spin measurements: Spin states are often the simplest example to discuss the weirdness of quantum mechanics.



left: Consider a sequence of Stern-Gerlach apparatuses, as shown on the left, but with different directions for the magnetic field inhomogeneity (pointing from S to N). Thus in the first magnet the force depends on $\hat{S}_z$ in the second on $\hat{S}_x$ and in the third again on $\hat{S}_z$.

For an atom that ended up in the top spot after magnet 1, we know the spin state was $|\uparrow\rangle$. If we now would immediately measure $\hat{S}_z$ again, the probability to find $-\hbar/2$ would be zero. What happens in the second magnet?
We can use Eq. (4.114) to write $|\uparrow\rangle = (|\leftarrow\rangle + |\rightarrow\rangle)/\sqrt{2}$. Using postulate III in section 3.6 we thus know that the second magnet will measure $\hat{S}_x \simeq +\hbar/2$ (left spot) with probability 1/2 and $\hat{S}_x \simeq= -\hbar/2$ (right spot) also with probability 1/2. Now lets use the third Stern-Gerlach magnet on the left spot, where atoms were in $|\leftarrow\rangle = (|\uparrow\rangle + |\downarrow\rangle)/\sqrt{2}$. Applying postulate III in section 3.6 again, we deduce a 50-50 probability for either spin up or spin down, even though after the first magnet the probability for down was zero!!! Apparently the measurement of x in between has messed things up. It did that because $\left[\hat{S}_x, \hat{S}_z\right] \neq 0$.

The scenario in section 39 is really similar to the sequence discussed in example 24, but since the Hilbert-space for spin-1/2 is only two dimensional, the spin-example is much neater.

4.7.3 Spin versus orbital angular momentum

We have introduced spin as being "like an angular momentum", but without the interpretation of something spinning or orbiting. To clarify, we list here an overview table contrasting the two types of angular momentum in quantum mechanics, orbital (external) and spin (intrinsic): We have marked the only instances where the behaviour of a spin differs from that of an orbital angular momentum in red above. Together with the fact that spin and orbital angular momentum experimentally appear conserved only in combination, we conclude that spin is an intrinsic property of fundamental particles that behaves in every relevant way like an angular momentum, hence is an angular momentum.

4.7.4 Pseudospin

Regardless of what the actual states are, any quantum mechanical system that has only two-states could be described with a vector representation of the form (4.109) and all operators on these states can be written in terms of Pauli matrices (4.112). When using this approach, one talks of a "pseudo-spin" system. That means the degree of freedom might actually not be a spin, but the math can all be handled by "thinking of" a spin system. The approach is most common for $s = 1/2$ and two-state systems, but also works for more states and higher spins.

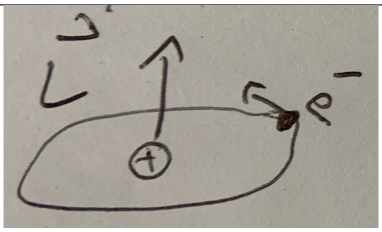
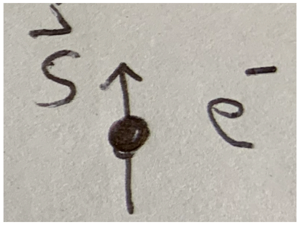
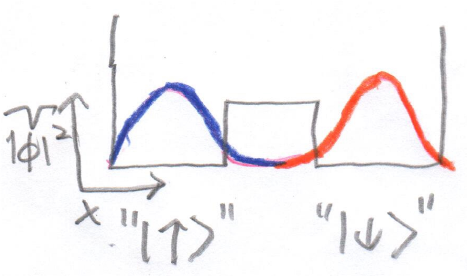
<table>
<tr><th colspan="2">Angular momentum</th></tr>
<tr><th>Orbital Angular Momentum</th><th>Intrinsic Angular Momentum (Spin)</th></tr>
<tr><td>
(careful “classical” picture)</td><td>
(careful “wrong” picture)</td></tr>
<tr><td>$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar \hat{L}_z$</td><td>$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar \hat{S}_z$</td></tr>
<tr><td>$\hat{\mathbf{L}}^2 \vert\, \ell m_\ell \,\rangle = \hbar^2 \ell(\ell+1) \vert\, \ell m_\ell \,\rangle$</td><td>$\hat{\mathbf{S}}^2 \vert\, s m_s \,\rangle = \hbar^2 s(s+1) \vert\, s m_s \,\rangle$</td></tr>
<tr><td>$\hat{L}_z \vert\, \ell m_\ell \,\rangle = \hbar m_\ell \vert\, \ell m_\ell \,\rangle$</td><td>$\hat{S}_z \vert\, s m_s \,\rangle = \hbar m_s \vert\, s m_s \,\rangle$</td></tr>
<tr><td>$\ell = 0, 1, 2, 3, \ldots$</td><td>$s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$</td></tr>
<tr><td>$-\ell \leq m_\ell \leq l$</td><td>$-s \leq m_s \leq s$</td></tr>
<tr><td>$\hat{\mathbf{L}} = -i\hbar \left(\mathbf{e}_\varphi \frac{\partial}{\partial \theta} - \mathbf{e}_\theta \frac{1}{\sin\theta} \frac{\partial}{\partial \varphi} \right)$ Eq. (4.36)</td><td>$\nexists$</td></tr>
<tr><td colspan="2">Conserved only together, Total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{S}} + \hat{\mathbf{L}}$.</td></tr>
</table>

Table 3: Table of similarities and differences between orbital angular momentum and spin-angular momentum.

Example 40, Coupled quantum dots: Consider two coupled quantum dots as seen in the Assignment.



left: For a more gentler design than in that assignment, we can realize a scenario where the particle is only ever in the ground-state of the left well $\phi_{1L}(x)$, or the ground state of the right well $\phi_{1R}(x)$. We can then write the wavefunction as $\Psi(x,t) = c_L(t)\phi_{1L}(x) + c_R(t)\phi_{1R}(x)$. If we simply label $\phi_{1L}(x) \simeq |\uparrow\rangle$ and $\phi_{1R}(x) \simeq |\downarrow\rangle$, we can write this as $\Psi(x,t) = c_L(t)|\uparrow\rangle + c_R(t)|\downarrow\rangle$, but really there is not ever a spin in the picture. Only a pseudo-spin, the meaning of which we have to carefully define.

Example 41, Q-Bits: Quantum computers are based on a Q-bit, which is any quantum state with only two basis states

$$|\,\Psi\,\rangle = c_0|\,0\,\rangle + c_1|\,1\,\rangle. \tag{4.115}$$

A Q-bit is more powerful than a classical bit, since it can carry not only the information 0 versus 1 but c_0 and c_1 (i.e. complex numbers). We know from (4.108) that this could be the actual spin 1/2 of a particle, but more often one uses (meta-)stable internal states of atoms and ions, or even current quantum states of superconducting circuits.

4.8 Addition of Angular momenta

We just learnt that the electron carries intrinsic angular momentum, called spin, and learnt earlier in week 8 to 10 that it may also carry orbital angular momentum. More complex atoms than Hydrogen additionally have multiple electrons. Angular momentum is conserved only "alltogether", so we need to be able to add quantum mechanical angular momenta.

We assume there are two particles, labelled 1 and 2, having spin s_1 and s_2 respectively. The first one has a spin state $|\, s_1, m_{s1} \,\rangle$ and the second $|\, s_2, m_{s2} \,\rangle$. We had seen in section 4.1.3 briefly, that a state describing the position of two particles gets one position variable for each. Similarly a state describing the spin of two particles, now gets the full set of spin quantum numbers for each.

We write a

Two particle spin state

$$|\, s_1, m_{s1}; s_2, m_{s2} \,\rangle = |\, s_1, m_{s1} \,\rangle \otimes |\, s_2, m_{s2} \,\rangle, \tag{4.116}$$

where $\otimes$ is the tensor product.

- We now have two spin operators, $\hat{\mathbf{S}}_1$ for particle 1 and $\hat{\mathbf{S}}_2$ for particle 2. The simplest way to understand the above state (without having to worry about the technicality "tensor product"), is to define the state through the (hopefully logical) action of those spin operators:

$$\begin{aligned}
\hat{\mathbf{S}}_1^2 |\, s_1, m_{s1}; s_2, m_{s2} \,\rangle &= \hbar^2 s_1(s_1+1) |\, s_1, m_{s1}; s_2, m_{s2} \,\rangle, \\
\hat{S}_{z1} |\, s_1, m_{s1}; s_2, m_{s2} \,\rangle &= \hbar m_{s1} |\, s_1, m_{s1}; s_2, m_{s2} \,\rangle, \\
\hat{\mathbf{S}}_2^2 |\, s_1, m_{s1}; s_2, m_{s2} \,\rangle &= \hbar^2 s_2(s_2+1) |\, s_1, m_{s1}; s_2, m_{s2} \,\rangle, \\
\hat{S}_{z2} |\, s_1, m_{s1}; s_2, m_{s2} \,\rangle &= \hbar m_{s2} |\, s_1, m_{s1}; s_2, m_{s2} \,\rangle.
\end{aligned} \tag{4.117}$$

Tensor product (bonus): (simplified version). Given an arbitrary vector $\mathbf{v} \in \mathcal{V}$ in an N-dimensional vector space $\mathcal{V}$, with components v_n, and another vector $\mathbf{w} \in \mathcal{W}$ in an M-dimensional vector space $\mathcal{W}$, you can think of the tensor product $\otimes$ of these vectors as an $N \times M$ matrix

$$\mathbf{v} \otimes \mathbf{w} = \begin{bmatrix} v_1 w_1 & v_1 w_2 & \cdots & v_1 w_M \\ v_2 w_1 & v_2 w_2 & \cdots & v_2 w_M \\ \vdots & \vdots & \ddots & \vdots \\ v_N w_1 & v_N w_2 & \cdots & v_n w_M \end{bmatrix} \tag{4.118}$$

The space of all these matrices is itself a vector-space again, written $\mathcal{V} \otimes \mathcal{W}$, and called the tensor product of $\mathcal{V}$ and $\mathcal{W}$. We can repeat the operation to add a third "dimension" to the matrix (making it a cube of numbers, rather than a square) etc., thus generating even higher dimensional objects than Matrices (ND arrays).
After forming (4.118) we can turn $\mathbf{v} \otimes \mathbf{w}$ again into a vector (in a $N \times M$ dimensional space), by reshaping:

$$\mathbf{v} \otimes \mathbf{w} = \begin{bmatrix} v_1 w_1 & v_1 w_2 & \cdots & v_1 w_M & v_2 w_1 & v_2 w_2 & \cdots & v_n w_{M-1} & v_n w_M \end{bmatrix}^T . \tag{4.119}$$

- For a more rigorous mathematical definition, see math courses.
- For the present course, knowing the dotpoint above the yellow box should be sufficient.

From the two single spin operators, we can define

Total spin operators

$$\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2. \tag{4.120}$$

From this we find $\hat{S}_z = \hat{S}_{z1} + \hat{S}_{z2}$ and

$$\hat{S}^{\pm} = \hat{S}_1^{\pm} + \hat{S}_2^{\pm}. \tag{4.121}$$

- Here $\hat{\mathbf{S}}$ describes the total spin of the two particles, and hence $\hat{S}_z$ the total z-component.
- Using the definition (4.106) to find ladder operators for the total spin, we can see that these decompose into ladder operators for the sub-spins.

Now we want to find what the action of the total spin operators (4.120) onto basis states such as (4.116) is, in order to re-label those with some quantum numbers that pertain to the total spin, instead of the individual spins. For the z-component, this is easy:

$$\hat{S}_z | s_1, m_{s1}; s_2, m_{s2} \rangle = (\hat{S}_{z1} + \hat{S}_{z2}) | s_1, m_{s1}; s_2, m_{s2} \rangle \overset{Eq.\ (4.117)}{=} \hbar \underbrace{(m_{s1} + m_{s2})}_{\equiv m_s} | s_1, m_{s1}; s_2, m_{s2} \rangle. \tag{4.122}$$

Apparently the state is an eigenstate of $\hat{S}_z$ with eigenvalue $\hbar m_s$ where $m_s = m_{s1} + m_{s2}$ is the quantum number for the total z-component. Unfortunately $\hat{\mathbf{S}}^2$ turns out a little more complicated. We follow Griffith and sort this with the example of

Example 42, Addition of two spin 1/2: We can use the notation of section 4.7.2. The advantage of $s_1 = s_2 = 1/2$ is that it is easy to list all the possible spin states of the kind (4.116), and their resultant total m_s:

$$\begin{aligned}
|\, s_1 = \frac{1}{2}, m_{s1} = \frac{1}{2}; s_2 = \frac{1}{2}, m_{s2} = \frac{1}{2}\,\rangle &= |\!\uparrow\uparrow\rangle, \quad m_s = 1,\\
|\, s_1 = \frac{1}{2}, m_{s1} = \frac{1}{2}; s_2 = \frac{1}{2}, m_{s2} = -\frac{1}{2}\,\rangle &= |\!\uparrow\downarrow\rangle, \quad m_s = 0,\\
|\, s_1 = \frac{1}{2}, m_{s1} = -\frac{1}{2}; s_2 = \frac{1}{2}, m_{s2} = \frac{1}{2}\,\rangle &= |\!\downarrow\uparrow\rangle, \quad m_s = 0,\\
|\, s_1 = \frac{1}{2}, m_{s1} = -\frac{1}{2}; s_2 = \frac{1}{2}, m_{s2} = -\frac{1}{2}\,\rangle &= |\!\downarrow\downarrow\rangle, \quad m_s = -1.
\end{aligned} \tag{4.123}$$

Given that the total z-component ranges over $m_s = -1, 0, 1$ and considering our earlier rules $-\ell \leq m \leq \ell$, we might suspect that a total angular momentum (spin) of $s = 1$ is in the picture. But we have one state too many.

To figure out why, let us successively apply the total lowering operator $\hat{S}^-$ from (4.121) to the state $|\!\uparrow\uparrow\rangle$. In the first step we find

$$\hat{S}^-|\!\uparrow\uparrow\rangle \overset{Eq.\ (4.121)}{=} \left(\hat{S}_1^-|\!\uparrow\rangle\right)|\!\uparrow\rangle + |\!\uparrow\rangle\left(\hat{S}_2^-|\!\uparrow\rangle\right) \overset{Eq.\ (4.106)}{=} (\hbar|\!\downarrow\rangle)\,|\!\uparrow\rangle + |\!\uparrow\rangle\,(\hbar|\!\downarrow\rangle)\,. \tag{4.124}$$

Fixing the normalisation again[a], we write the resultant state as $(|\!\uparrow\downarrow\rangle + |\!\downarrow\uparrow\rangle)/\sqrt{2}$. Applying $\hat{S}^-$ one more time gets us into $|\!\downarrow\downarrow\rangle$ and any further time gives 0 (exercise). What happened to the fourth state from (4.123)? We can form one more linear combination out of the middle ones: $(|\!\uparrow\downarrow\rangle - |\!\downarrow\uparrow\rangle)/\sqrt{2}$. Here, applying either $\hat{S}^-$ or $\hat{S}^+$ gives zero (exercise). This looks suspiciously like angular momentum zero: $s = 0$, for which the only allowed m_s would be zero.

---

[a] The rule for many-body states is: whenever the quantum numbers are different for any of the constituents, the states are orthogonal. E.g. $\langle\uparrow\uparrow|\uparrow\downarrow\rangle = 0$

Example continued: You can indeed show (Griffith), that $\hat{\mathbf{S}}^2|\uparrow\uparrow\rangle = \hbar^2 s(s+1)|\uparrow\uparrow\rangle$ with $s = 1$ and similarly for the other two states we obtained above by applying the lowering operator, while $\hat{\mathbf{S}}^2(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2} = 0$. We call the former three triplet states and the last one singlet state, and can now re-relabel them as originally planned with quantum numbers s and m_s for the combined spin state:

$$\begin{aligned}
|\, s=1, m_s=1\,\rangle &= |\uparrow\uparrow\rangle, \\
|\, s=1, m_s=0\,\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \\
|\, s=1, m_s=-1\,\rangle &= |\downarrow\downarrow\rangle, \\
|\, s=0, m_s=0\,\rangle &= \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle).
\end{aligned} \tag{4.125}$$

Effectively switching between $|\, s m_s\,\rangle$ and $|\, s_1, m_{s1}; s_2, m_{s2}\,\rangle$ is just a basis change from an individual spin basis to a combined spin basis.

Without doing the proof for that, we now state the result for any other values of s_1 and s_2:

General addition of spins When describing two spins s_1 and s_2 with a combined basis, the total spin quantum number s can vary over the entire range:

$$s = s_1 + s_2, s_1 + s_2 - 1, \cdots, |s_1 - s_2|, \tag{4.126}$$

in integer steps. For a given s, the z-component quantum number m_s takes the usual range $-s \leq m_s \leq s$.
We can always write the combined basis states as a sum of the individual basis states:

$$|\, s\, m_s\,\rangle = \sum_{m_{s1}, m_{s2}; m_{s1}+m_{s2}=m_s} C^{(s_1 s_2; s)}_{(m_{s1}, m_{s2}; m_s)} |\, s_1, m_{s1}; s_2, m_{s2}\,\rangle \tag{4.127}$$

where the coefficients $C^{(s_1 s_2; s)}_{(m_{s1}, m_{s2}; m_s)}$ are called Clebsch-Gordon coefficients.

- While we wrote “addition of spins“ in the above, the same scheme works for the addition of orbital angular momenta $\hat{\mathbf{L}}_1$ and $\hat{\mathbf{L}}_2$ or the addition of an orbital angular momentum $\hat{\mathbf{L}}$ and a spin $\hat{\mathbf{S}}$.
- You can find algorithms on how to calculate any Clebsch-Gordon coefficients in the more advanced books. Or you might nowadays just want to use an online calculator for them, such as e.g. https://www.volya.net/index.php?id=vc .
- You can visualise the range (4.126) somewhat through the addition of 3D vectors: The magnitude of $\mathbf{v} = \mathbf{w}_1 + \mathbf{w}_2$ is largest when the two constituent vectors are parallel, in which case $|\mathbf{v}| = |\mathbf{w}_1| + |\mathbf{w}_2|$. It is smallest when they are antiparallel, in which case $|\mathbf{v}| = |\mathbf{w}_1| - |\mathbf{w}_2|$ if $|\mathbf{w}_1| > |\mathbf{w}_2|$. You can find diagrams carrying this visualisation further in many books.

Week 12

PHY 303 Quantum Mechanics
Instructor: Sebastian Wüster, IISER Bhopal, 2023

These notes are provided for the students of the class above only. There is no guarantee for correctness, please contact me if you spot a mistake.

5 Two particle quantum mechanics

We had already taken a first glimpse at how to handle more than one particle in quantum mechanics in section 4.1.3 and section 4.6.1. Let us explore this a bit more, to introduce some of the most fundamental and far reaching implications.

We had already given a generic Hamiltonian for two non-interacting particles in (4.28). When there are no interactions, we can again make a product Ansatz in the two particle wavefunction (5.2), writing

$$\psi(\mathbf{r}_a, \mathbf{r}_b) = \phi(\mathbf{r}_a)\eta(\mathbf{r}_b), \tag{5.1}$$

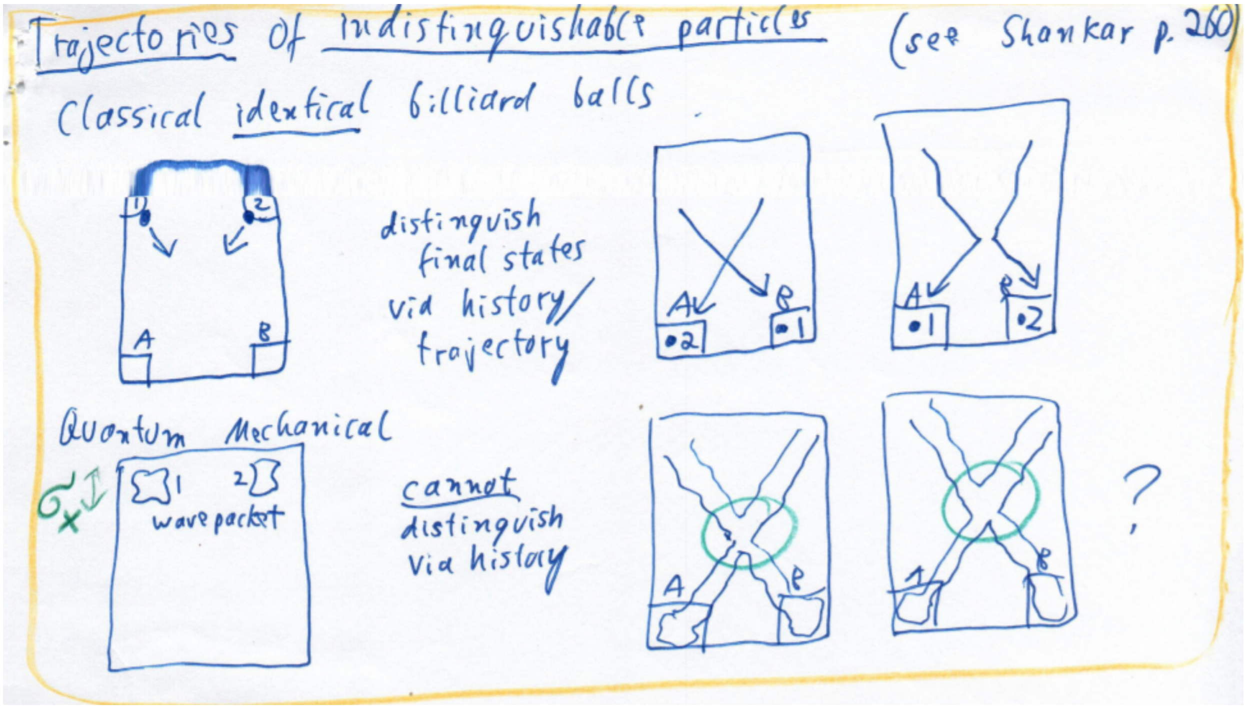
perform separation of variables on the TISE that follows from the Hamiltonian (4.28) and reach two independent TISEs:

$$\begin{aligned} \left[-\frac{\hbar^2}{2m_a}\Delta_{\mathbf{r}_a} + V(\mathbf{r}_a)\right]\phi(\mathbf{r}_a) &= E_a\phi(\mathbf{r}_a), \\ \left[-\frac{\hbar^2}{2m_b}\Delta_{\mathbf{r}_b} + V(\mathbf{r}_b)\right]\eta(\mathbf{r}_b) &= E_b\eta(\mathbf{r}_b). \end{aligned} \tag{5.2}$$

Suppose each Hamiltonian has quantised eigenstates $\phi_n(\mathbf{r}_a)$, $\eta_m(\mathbf{r}_b)$, a joint solution could be $\Psi_{nm}(\mathbf{r}_a, \mathbf{r}_b) = \phi_n(\mathbf{r}_a)\eta_m(\mathbf{r}_b)$, which we would reasonably interpret as corresponding to "particle a is in state n and particle b is in state m". However this idea runs into some fundamental trouble:

5.1 Indistinguishable particles

How would you distinguish two identical fundamental particles? I.e. two electrons in the same spin state? The answer is you cannot, since there is no additional label you can flag it with. In classical mechanics, you could in principle distinguish even fully identical objects a and b via their position history $\mathbf{r}_a(t)$ and $\mathbf{r}_b(t)$, but due to the HUP (1.47) this does not work in quantum mechanics, see diagram below:



]

- We conclude that a statement like "particle a is in state n and particle b is in state m" does not make sense for indistinguishable particles.
- All we could hope to say is "there is some particle in state n and another one in state m".
- This implies that mathematically, the wavefunction $\psi(\mathbf{r}_a, \mathbf{r}_b)$ must be equivalent to $\psi(\mathbf{r}_b, \mathbf{r}_a)$.
- In practice, we can often also deal with "distinguishable" particles in quantum mechanics, even if they are the same type of particle, as long as they never get too close to each other[16].

Since the overall phase or sign of a wave-function does not matter (see section 1.6.1), "being equivalent" still allows for a change in the complex phase. We thus demand $\psi(\mathbf{r}_a, \mathbf{r}_b) = e^{i\varphi}\psi(\mathbf{r}_b, \mathbf{r}_a)$. Swapping the position again then gives $\cdots = (e^{i\varphi})^2\psi(\mathbf{r}_a, \mathbf{r}_b)$. How we are back where we started, hence we need $(e^{i\varphi})^2 = 1$, which is true for $\varphi = 0, \pi$. We have thus shown the

Indistinguishable particle exchange symmetry

$$\psi\left(\mathbf{r}_a, \mathbf{r}_b\right) = \pm\psi\left(\mathbf{r}_b, \mathbf{r}_a\right). \tag{5.3}$$

The two-particle wavefunction for two indistinguishable particles must be symmetric or anti-symmetric under exchange of those two particles.

---

[16] Meaning their wavefunctions never overlapp

Example 43, (Anti-)symmetrized wavefunctions: Let us reconsider the state we had seen earlier $\Psi_{nm}(\mathbf{r}_a, \mathbf{r}_b) = \phi_n(\mathbf{r}_a)\eta_m(\mathbf{r}_b)$. Since particles are indistinguishable $m_a = m_b$ in (5.2) and ϕ_n and η_m really label the same set of eigenfunctions of a TISE. Let us thus use the label ϕ only: $\Psi_{nm}(\mathbf{r}_a, \mathbf{r}_b) = \phi_n(\mathbf{r}_a)\phi_m(\mathbf{r}_b)$. We can fix the symmetrisation issues by writing

$$\tilde{\Psi}_{nm}(\mathbf{r}_a, \mathbf{r}_b) = \frac{1}{\sqrt{2}}\left(\phi_n(\mathbf{r}_a)\phi_m(\mathbf{r}_b) \pm \phi_m(\mathbf{r}_a)\phi_n(\mathbf{r}_b)\right), \tag{5.4}$$

either way this now satisfies (5.3), but the meaning has changed from "particle a is in state n and particle b is in state m" to "there is some particle in state n and another one in state m" as required.

We also know which are which:

Bosons and Fermions Particles with integer spin $s = 0, 1, 2$ are called Bosons. They are the ones which have a symmetric many-body wavefunction, i.e. $\oplus$ in (5.3). Particles with half-integer spin $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ are called Fermions. They are the ones which have an anit-symmetric many-body wavefunction, i.e. $\ominus$ in (5.3).

- You can show this later in relativistic quantum mechanics, where the link between wavefunction symmetry and spin quantum number arises from the requirement to form a Lorentz invariant Hamiltonian where events outside the light-cone cannot affect each other. This is called spin-statistics theorem.
- Fundamental Fermions are all the matter particles, electrons, quarks and their higher generation counterparts as well as neutrinos. You can deduce from repeated applications of (4.126) that the combinations of an odd number of Fermions is a Fermion, while the combination of an even number of Fermions is a Boson. Thus also neutrons and protons are Fermions, since they contain three quarks. Then in turn, neutral atoms with an odd number of neutrons are also Fermions.
- Fundamental Bosons are all the force carriers photons, gluons, W and Z Bosons and the Higgs Boson. Composite Bosons are e.g. pions, $\pi^{0,\pm}$, which are bound states of a quark and an anti-quark. With the same argumentation as above, also neutral atoms with an even number of neutrons are Bosons.
- The most important difference between a Fermionic and a Bosonic wavefunction is at $\mathbf{r}_a = \mathbf{r}_b = \mathbf{r}$, i.e. when the particles try to be at the same place. For Bosons this is fine, for Fermions (5.3) gives you $|\psi\left(\mathbf{r}, \mathbf{r}\right)|^2 = 0$, i.e. there is zero probability for two Fermions to ever be in the same place.

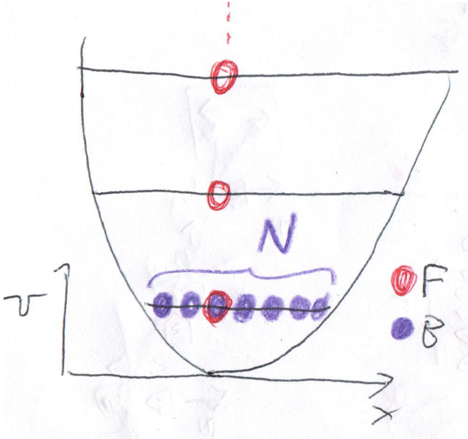
The perhaps most important consequence of the above is the

Pauli exclusion principle Two indistinguishable Fermions cannot occupy the same single particle quantum state ϕ_0.

- Both particle in the same state would be described by $\psi(r_a, r_b) = \phi_0(r_a)\phi_0(r_b)$, but that wavefunctions is not correctly anti-symmetric. We would have to write $\psi(r_a, r_b) = [\phi_0(r_a)\phi_0(r_b) - \phi_0(r_b)\phi_0(r_a)]/\sqrt{2} = 0$ in an attempt to a anti-symmetrize this to fulfill (5.3), but clearly this vanishes. Note that the tag "indistinguishable Fermions" only applies to particles in identical spin-states (otherwise you can distinguish them via the spin state).
- Pauli's exclusion principle and the Hydrogen states from section 4.6 are nearly enough to understand the periodic table of elements. The same calculations as in section 4.6 gives us the solutions for a single electron seeing a nuclear charge of $+Ze$ instead of $+e$, where Z is the number of protons in the nucleus. You just have to replace $e^2 \rightarrow Ze^2$ in all our solutions. Ignoring electron-electron interactions in a first step, you can then find all the eigenstates for heavier atoms using techniques as for Eq. (5.2) and the Pauli principle. The latter forces us to fill two electrons only, into each Hydrogen-like state. The primary way that electron-electron interactions show up, is through the concept of screening: The two electrons in e.g. the $|\,1s\,\rangle$ state of Lithium are much closer to the nucleus than the valence electron inserted into $|\,2s\,\rangle$. As a result they screen the nucleus for the valence electron, which thus sees an "effective nuclear charge" $Z_{\text{eff}} \approx 1$ instead of $Z = 3$. This explains the periodic recurrences of e.g. ionisation energies. For (much) more details we refer to PHY402 "Atomic and molecular physics", where you will discuss multi-electron atoms.

For Bosons, there is no problem in occupying the same quantum state. This allows for example a

Example 44, Bose-Einstein condensate: Consider N non-interacting Bosonic atoms in a 1D harmonic oscillator potential as shown below. Using the same statement as for (5.2) for those N atoms we find just one TISE such as Eq. (2.42) in section 2.3 for *each* of those atoms. The absolute ground-state thus clearly is $\psi(x_1, x_2, \cdots x_N) = \phi_0(x_1)\phi_0(x_2)\cdots\phi_0(x_N)$, with SHO ground-state $\phi_0(x)$ from Eq. (2.65).



left: Thus all N atoms are in the same single particle state ϕ_0. The resultant many-particle state ψ describes what is called a Bose-Einstein condensate. In contrast Fermionic atoms would fill oscillator quantum states one by one, see on the left. See more on this in PHY435 "quantum many body physics of degenerate gases".

The two different variants of many body wavefunctions give rise to fascinating and useful behaviour, that you can explore further in courses on super-conductivity (involving a Bose-Einstein condensate of cooper pairs), superfluidity, neutron stars (stabilised by the Pauli principle applied to neutrons) etc.

5.2 Entanglement

Let us in this section consider quantum systems that have two *distinguishable parts*, labelled a and b. We can then classify quantum-states into two classes.

Entangled and separable states We call a quantum state $\psi(\mathbf{r}_a, \mathbf{r}_b)$ for two particles a and b separable, if it can be written as a product of a state for particle a and particle b, e.g.

$$\psi(\mathbf{r}_a, \mathbf{r}_b) = \phi_a(\mathbf{r}_a)\phi_b(\mathbf{r}_b). \tag{5.5}$$

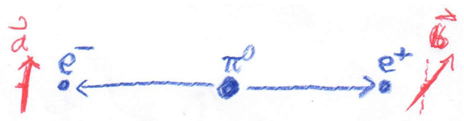
We call it entangled, if it cannot be written as a product, e.g.

$$\psi(\mathbf{r}_a, \mathbf{r}_b) = \frac{1}{\sqrt{2}}\left[\phi_a(\mathbf{r}_a)\phi_b(\mathbf{r}_b) - \phi_b(\mathbf{r}_a)\phi_a(\mathbf{r}_b)\right]. \tag{5.6}$$

- The easiest system in terms of which to think about entanglement, is a spin-1/2 object. In terms of the triplet and singlet states in (4.125), which are entangled and which are separable? (exercise).
- Entanglement is typically created through interactions of parts a and b.

Entangled states have some intriguing properties, which are best highlighted when considering the

EPR paradox Here EPR stands for Einstein-Podolsky-Rosen, who invented the paradox (in a slightly different guise) to show that quantum mechanics cannot simultaneously be real, local and complete.



left: A neutral pion π^0 can decay into an electron e^- and a positron e^+. Since the pion has spin $s = 0$, angular momentum conservation requires the two decay products to be in the spin-singlet state of Eq. (4.125): $|\,\psi\,\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$. In this state, neither electron nor proton has a well defined spin: A measurement of either will give ↑ or ↓ with 50% probability, on both particles (see postulate III in section 3.6).

However after we measured e.g. ↑ on the first particle, the state collapses according to postulate IV in section 3.6. In this case this means that $|\,\psi\,\rangle \rightarrow |\uparrow\downarrow\rangle$. Now we know the spin of the first and the second particle, so a measurement on the first seems to have affected the second. This argument applies even if the second particle is e.g. light-years away, causing EPR to conclude that something was "missing" in the quantum mechanical description of reality. There could be some "hidden variables" that explain the apparent weirdness.

The so-called paradox was ultimately resolved by

Bell's theorem Bell considered a more complicated version of the above, where spin is not measured only along the z-axis, but along two arbitrary axes in space **a** and **b**. Let's stick to just the z and x axes for the moment. Using our results Eq. (4.114), you can see that you can write the entangled state from example 5.2 also as $|\,\psi\,\rangle = (|\leftarrow\rangle|\rightarrow\rangle - |\rightarrow\rangle|\leftarrow\rangle)/\sqrt{2}$. So now if you randomly measure the spin along the x or z direction on one particle, the other one will always point opposite regardless of choice of measurement. How did it even "know" which axis we were going to measure?
Bell looked at the correlations $P(\mathbf{a},\mathbf{b}) = \langle\,\psi\,|(\mathbf{a}\cdot\hat{\mathbf{S}}_a)(\mathbf{b}\cdot\hat{\mathbf{S}}_b)|\,\psi\,\rangle$ and showed that the quantum mechanical result $P(\mathbf{a},\mathbf{b}) = -\mathbf{a}\cdot\mathbf{b}$ cannot be ever explained by a local hidden variable theory, who have to satisfy an inequality (Bell's inequality) that is violated by the quantum mechanical result. The quantum mechanical prediction was confirmed by many experiments since (first by Alain Aspect 1982, using entangled photons).

- The proof of Bell's theorem is not that hard, and can be found in Griffith, chapter 12. We refer to that also for more details on what is meant by locality, and by "hidden variable theories".

- Ultimately this is just another instance, where we have to abandon concepts from our everyday intuition in quantum mechanics. In quantum mechanics, it is simply impossible to individually, locally, describe two objects after they have interacted. In the example above, the interaction happens during the pion decay. Instead we have to describe them with a (usually entangled) two-body wavefunction such as (5.2), that ultimately is a highly non-local object once the two particles have moved far apart from each other.

- The experimental demonstration of quantum mechanical violations of Bell's inequality essentially solve the dispute between "realist" and "orthodox" interpretations mentioned in section 1.4 (and discussed much more in Griffith), in favor of the orthodox interpretation. Ascribing the particle(s) a pre-existing state prior to measurements would again require the use of some hidden variables.

- Bell's theorem also implies that entanglement is a stronger feature than classical correlations (since classical correlations are exactly what would be used in a hidden variable theory). It comes as no surprise then, that it is also the key resource based on which "quantum computers" can do tasks that classical computers cannot do in reasonable time.

This section again was more intended as an appetiser, you would get the main course on entanglement in courses on quantum information, quantum optics or entanglement itself.

The End