To be read along with chapter 2 in Hemmer, or selected sections from Bransden & Joachain.

TILLEGG 2

2. Fundamental principles

Chapter 2 in this course — Fundamental principles — is covered by "Tillegg 2", which you are now reading, together with chapter 2 in Hemmer's book. Most of this stuff is also covered in the book by Bransden & Joachain.

In this chapter, we formulate the basic principles of quantum mechanics and introduce some concepts and mathematical methods and remedies which are much used in this theory.

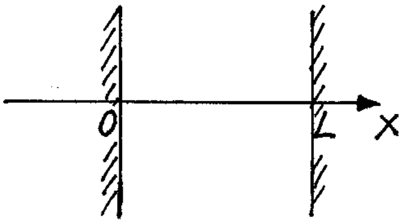
Some of this will in the beginning appear to be somewhat abstract and difficult to understand. To make it more concrete and easier to grasp, we start with a concrete example of a quantum-mechanical system, the simplest example of them all in fact. This is the system where a single particle is moving in an infinitely deep one-dimensional potential well, also called "particle in a box".

This example is not only very simple, but also a very important example in quantum mechanics. You will profit very much studying it thorougly.

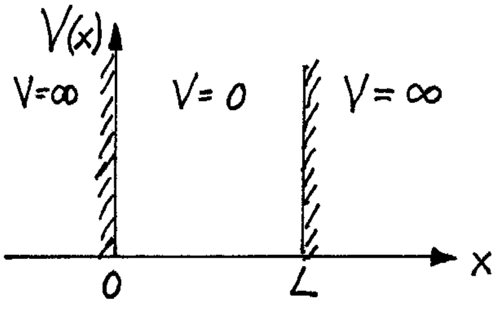
The sections marked by *** are not parts of the courses FY1006/TFY4215.

2.1 Particle in a box

2.1.a Outline of the problem



two impenetrable walls



potential diagram

This system consists of a particle with mass m moving between two impenetrable walls. The potential (the potential energy) is zero *between* the walls and infinite outside the well:

$$V(x) = \begin{cases} 0 & \text{for} \quad 0 < x < L, \\ \infty & \text{for} \quad x < 0 \quad \text{and} \quad x > L. \end{cases}$$

For this so-called one-dimensional box potential we neglect the motion in the y and z directions. The classical expression for the energy then is

$$E = K + V = \frac{p_x^2}{2m} + V(x).$$

According to Schrödinger's recipe (see section 1.7.a in Tillegg 1), this classical energy expression corresponds to an energy *operator* (Hamiltonian)

$$\widehat{H} = \widehat{K} + V(x) = \frac{\widehat{p}_x^2}{2m} + V(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$$

We want to find all the **stationary solutions** of the Schrödinger equation,

$$\boxed{i\hbar\,\frac{\partial\Psi(x,t)}{\partial t} = \widehat{H}\Psi(x,t)} \qquad \left(\begin{array}{l}\text{the time-}\underline{\text{dependent}}\\ \text{Schrödinger equation}\end{array}\right), \tag{T2.1}$$

that is, all soulutions on the form

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}. \tag{T2.2}$$

Inserting (T2.2) into (T2.1) we then get the following equation for the **spatial part of the wave function** $\psi(x)$:

$$\boxed{\begin{array}{c}\widehat{H}\psi(x) = E\psi(x), \qquad \text{or}\\[1ex] \left[-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\psi(x).\end{array}} \tag{T2.3}$$

This is **Schrödinger's time-<u>independent</u> equation** in one dimension.

This equation tells us that the spatial part $\psi(x)$ of the stationary solution (T2.1) must be an eigenfunction of the Hamiltonian operator $\widehat{H}$. Thus, our task is to find *all* such **energy eigenfunctions**.

For $x < 0$ and for $x > L$, where the potential is infinite, these energy eigenfunctions must all be equal to zero. It can be shown that this follows from (T2.3). Later we shall also see from this equation that the energy eigenfunctions must be continuous for all x.

2.1.b Energy quantization

For $0 < x < L$ the potential is equal to zero, and (T2.3) takes the form

$$\psi'' = \frac{2m}{\hbar^2}[V(x) - E]\psi = -\frac{2mE}{\hbar^2}\,\psi.$$

Here, ψ'' is the **curvature** of ψ. The *relative* curvature thus is

$$\psi''/\psi = -\frac{2mE}{\hbar^2}.$$

For $E < 0$ we thus have $\psi''/\psi > 0$, and ψ must curve (bend) *outwards* from the x axis (actually as a linear combination of $\sinh \kappa x$ and $\cosh \kappa x$, where $\kappa = \sqrt{-2mE/\hbar^2}$). But then it is impossible to satisfy the continuity conditions $\psi(0) = \psi(L) = 0$. This shows that negative energy eigenvalues do not exist for this potential, as we also expect from classical considerations.

For $E = 0$ we have $\psi'' = 0$, so that $\psi(x) = Ax + B$. The continuity condition $\psi(0) = \psi(L) = 0$ then gives $\psi(x) = 0$, which is of course totally useless as an energy eigenfunction (cf the probability interpretation of the wave function). So here we get a surprise compared to classical mechanics: Quantum mechanics (the Schrödinger equation) does not allow the particle to be at rest between the two walls; the kinetic energy has to be positive.

For $E > 0$, the eigenvalue equation (T2.3) takes the form

$$\psi'' = -\frac{2mE}{\hbar^2}\,\psi \equiv -k^2\psi, \qquad k \equiv \frac{1}{\hbar}\sqrt{2mE}.$$

The general solution now is sinelike with wave number k:

$$\psi(x) = A\sin kx + B\cos kx \qquad \left(E = \frac{\hbar^2 k^2}{2m}\right).$$

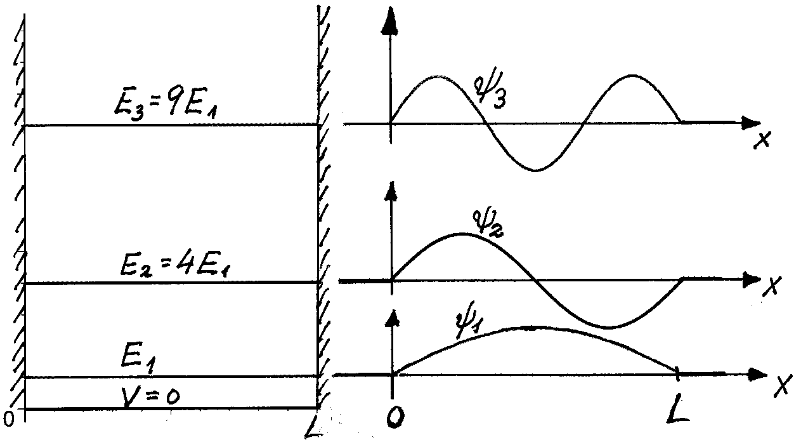
The continuity conditions give

$$\psi(0) = \underline{B = 0} \qquad \text{and} \qquad \psi(L) = A\,\underline{\sin kL = 0}.$$

(Here, A must be different from zero.) The condition $\sin kL = 0$ means that kL is an integer multiple of π, and implies that $\psi(x)$ inside the box consists of an integer number of half wavelengths (half periods of the sine). Thus we arrive at the following surprising conclusion: The wave number k and the energy are **quantized**:

$$k_n = n\,\frac{\pi}{L}, \qquad E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2\pi^2}{2mL^2}\,n^2, \quad n = 1, 2, \cdots. \tag{T2.4}$$

We shall see that energy quantization is characteristic for all bound states. This example shows that the quantization follows from the fact that the Schrödinger equation is a *wave equation*; it is due to the *wave nature* of the particle.



The ground state (per definition the state with the lowest energy) is as we see a half-wave, with energy

$$E_1 = \frac{\hbar^2\pi^2}{2mL^2}.$$

This is the lowest energy that the particle between the walls is allowed to have. We note that this minimal energy increases with decreasing mass, and that it also increases with decreasing box width L. So the smaller space we give the particle, the higher energy it is *forced to have*, because of its wave nature. I use to call this "quantum wildness"; the smaller the cage, the wilder the tiger becomes.

2.1.c Zeros (nodes), symmetry and curvature properties

We note that the number of zeros (excluding the two for $x = 0$ and $x = L$) is $n-1$; the ground state has no zero, the first excited state has one, and so on. This is a characteristic property of bound states in one-dimensional potentials; the number of zeros increases with the energy. This is also easily understood from the expression for the relative curvature of the energy eigenfunctions,

$$\frac{\psi''}{\psi} = -\frac{2m}{\hbar^2}\left[E - V(x)\right] = -\frac{2mE}{\hbar^2} \;:$$

Increasing (kinetic) energy means larger ψ''/ψ, that is faster curvature and hence more zeros.

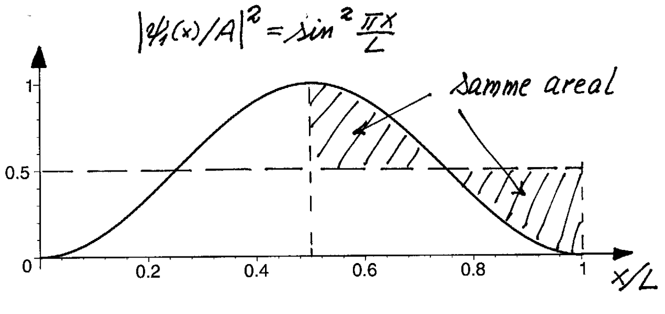
We should note that the box potential is symmetric with respect to the midpoint of the potential, $x = L/2$. This actually is the reason that ψ_1, ψ_2, ψ_3, ψ_4 etc are respectively symmetric, antisymmetric, symmetric, antisymmetric etc with respect to the midpoint. We shall see later that this is a general property of energy eigenstates in a symmetric one-dimensional potential.

2.1.d Normalization, probability density

If we want to interpret $|\psi(x)|^2$ as the probability *density*, so that $|\psi(x)|^2dx$ is the probability of finding the particle in the interval $[x, x + dx]$, we must require that

$$\boxed{\int_0^L |\psi(x)|^2 dx = 1.} \qquad \begin{pmatrix}\text{normalization}\\ \text{condition}\end{pmatrix}, \qquad \text{(T2.5)}$$

The figure shows $|\psi_1(x)/A|^2 = \sin^2 \pi x/L = \frac{1}{2}(1 - \cos 2\pi x/L)$.



probability density for the ground state

Here we see that the probability density for the ground state contains one period of the cosine, which therefore does not contribute to the integral. The same holds for the first excited state, which contains two periods, etc. Thus we can conclude that the average over the box of $\sin^2 n\pi x/L$ equals one half, as indicated in the figure. The normalization condition therefore gives

$$1 = |A|^2 \int_0^L \sin^2 \frac{n\pi x}{L}\, dx = |A|^2 \cdot \tfrac{1}{2} \cdot L \qquad \Longrightarrow \qquad |A| = \sqrt{\frac{2}{L}}.$$

We then obtain a normalized wave function by setting

$$A = e^{i\beta}\sqrt{\frac{2}{L}},$$

where the phase β can be chosen arbitrarily. A simple choice is $\beta = 0$. This freedom in the choice of a phase factor holds in general when we want to normalize a wave function. This means of course that the factor $e^{i\beta}$ in the wave function doesn't mean anything physically; it drops out in the calculation of quantities like the probability density $|\psi_n(x)|^2$ and expectation values like

$$\left\langle\, x^k \,\right\rangle_{\psi_n} = \int x^k |\psi_n(x)|^2 dx.$$

With the above choice, the normalized stationary states and the energy eigenfunctions of the box are

$$\Psi_n(x,t) = \psi_n(x) e^{-iE_n t/\hbar}, \quad \psi_n(x) = \sqrt{\frac{2}{L}}\,\sin k_n x, \quad k_n = \frac{n\pi}{L}, \quad E_n = \frac{\hbar^2 k_n^2}{2m}, \quad n = 1, 2, \cdots. \tag{T2.6}$$

Note that the constant in front is *not* determined by the eigenvalue equation; we find it using the normalization condition.

> **A small exercise:** As we have seen, the energy eigenfunctions alternate between being symmetric and antisymmetric wit respect to the "symmetry point" of the box, which is the midpoint $x = L/2$. The symmetry properties of the eigenfunctions ψ_1, ψ_2 and ψ_3 are obvious in the diagrams on page 3 but, if you choose a different coordinate system, with the origin ($x' = 0$) in the middle of the box, then the symmetry properties will become clear also in the expressions $\psi_1(x')$, $\psi_2(x')$ and $\psi_3(x')$ for the three eigenfunctions.
> **a.** Does the change of coordinate system imply any change of the *wave numbers* k_1, k_2 and k_3 for the three eigenfunctions?
> **b.** Find the expressions $\psi_1(x')$, $\psi_2(x')$ and $\psi_3(x')$, and check if the symmetry properties emerge as they should. [Hint: $\cos kx'$ and $\sin kx'$ are respectively symmetric and antisymmetric.]

2.1.e Orthogonality

It is easy to see that for example $\psi_1(x)$ and $\psi_2(x)$ are **orthogonal**. With this we mean that

$$\langle\, \psi_1, \psi_2 \,\rangle \equiv \int_0^L \psi_1^*(x)\psi_2(x) dx = 0.$$

Later we shall see that this can be generalized:

$$\langle\,\psi_n,\psi_k\,\rangle \equiv \int_0^L \psi_n^*(x)\psi_k(x)dx = \left\{\begin{array}{lll} 1 & \text{for} & n=k \\ 0 & \text{for} & n\neq k \end{array}\right\} \equiv \delta_{nk}. \tag{T2.7}$$

When the energy eigenfunctions are both orthogonal and normalized, we say that they are a **set of orthonormalized functions**.

2.1.f Discussion

Classically, a particle with energy E will travel back and forth between the two walls with a velocity $v_x = \pm\sqrt{2E/m}$. There is a striking contrast between such a classical state of motion and the properties of the stationary states we have studied above. We note that the probability densities of the stationary states,

$$|\Psi_n(x,t)|^2 = |\psi_n(x)|^2, \tag{T2.8}$$

are time independent, and also symmetric with respect to the midpoint of the box. This implies that the expectation value of the position x is equal to $L/2$. Later we shall see that the expectation values of p_x (and hence of v_x) are equal to zero for all the stationary states. So there there really *is* "something stationary" about the stationary states.

Then we must of course ask if quantum mechanics only desribes states where "nothing happens"? The answer is no. This is because the stationary states are *not the only* solutions of the Schrödinger equation. Because this equation is both linear and homogeneous, we can easily convince ourselves that

If $\Psi_a(x,t)$ and $\Psi_b(x,t)$ are two solutions of the time-dependent Schrödinger equation, then also the linear combination

$$\Psi(x,t) = c_1\Psi_a(x,t) + c_2\Psi_b(x,t)$$

is a solution. Here, c_a and c_b are arbitrary complex coefficients.

$$\left(\begin{array}{c}\text{superposition}\\ \text{principle}\end{array}\right) \tag{T2.9}$$

The most general wave function for the particle in the box therefore is

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\Psi_n(x,t) = \sum_{n=1}^{\infty} c_n e^{-iE_nt/\hbar}\psi_n(x). \tag{T2.10}$$

Since this wave function does not have the form (T2.2), it describes a **non-stationary** state. By the use of the orthonormality condition (T2.7) it can be shown that the normalization condition for this non-stationary state is [1]

$$1 = \int \Psi^*(x,t)\Psi(x,t)dx = \cdots = \sum_{n=1}^{\infty} |c_n|^2. \tag{T2.11}$$

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[1] The product of the two sums $\Psi(x,t)$ and $\Psi^*(x,t)$ contains a number of cross terms which integrate to zero because of the orthogonality. The integrals over the remaining terms, the "square" terms, essentially are the normalization integrals.

For such a non-stationary state, the expectation values of the position and the momentum will depend on the time, so in such a state things "happen".

> The Matlab program "box_non_stationary.m" shows an example, with a 50/50 superposition of the stationary solutions of the ground state and one of the excited states:
>
> $$\Psi(x,t) = \frac{1}{\sqrt{2}}\Psi_1(x,t) + \frac{1}{\sqrt{2}}\Psi_{n2}(x,t).$$
>
> You can choose the quantum number $n2$ yourself when running this program. The animation shows how the probability density $|\Psi(x,t)|^2$ and the expectation value $\langle\, x \,\rangle$ of the position "move" as functions of time.
>
> With a superposition of *several* stationary states (with a suitable choice of the coefficients c_n) we may also construct a wavefunction $\Psi(x,t)$ with the form of a wavepacket which mimics the classical motion of a particle which bounces back and forth between the two hard walls. You will find such an animation in the Matlab program "wavepacket_in_box".

Some of the "moral" of this discussion is: Since the most general quantum-mechanical state is a superposition of stationary solutions, the starting point for the treatment of any system is to find all possible energy eigenstates (and hence the stationary solutions) for the system.

> **Another point:** Some people worry about the zeros (nodes) in the wave functions and the probability densities of the stationary states. Thus the first excited state, for example, has a zero at the midpoint of the box: — "How can the particle manage to move from the left half of the box to the right half when $\Psi_2(x,t)$ and $|\Psi_2(x,t)|^2$ are equal to zero at the midpoint?" — Answer: Rewriting the sinus as $\sin k_2x = (e^{ik_2x} - e^{-ik_2x})/2i$, we see that the stationary state Ψ_2 can be written as a "50/50" superposition of two de Broglie waves:
>
> $$\Psi_2(x,t) = \frac{\sqrt{2/L}}{2i}\left(e^{i(k_2x - E_2t/\hbar)} - e^{i(-k_2x - E_2t/\hbar)}\right).$$
>
> This means that the zero is caused by destructive interference between the two de Broglie waves. The zero thus is a consequence of the wave nature, and is as natural as the zeros encountered in the double-slit experiment.

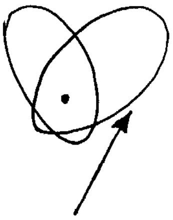
2.2 Basic postulates (Hemmer 2.1, B&J)

After the introductory chapter and the above particle-in-a-box example, we shall now try to formulate a set of postulates, upon which quantum mechanics can be built as a theory. These postulates play a role analogous to that of Newton's laws in classical mechanics. Which postulates to choose, and how to formulate them, is to some extent a matter of taste. In this course we follow Hemmer. Similar formulations can be found in B&J. Here we add the following comments:

2.2.a Postulate A (The operator postulate)

In trying to learn quantum mechanics, it is important that we learn to distinguish on one hand between the *physical system* and the quantities which can be measured (the **observables** of the system) — and on the other hand the concepts and the mathematical objects we use in the *theretical* quantum-mechanical description.

Physical system: Theoretical object:



observabel F $\Longleftrightarrow$ linear operator $\widehat{F}$

The operator postulate states that

$$\boxed{\text{To each observable physical quantity } F \text{ there corresponds in quantum-mechanical theory a linear operator } \widehat{F}.} \qquad \text{(T2.12)}$$

In this course we stick to the so-called **position-space formulation** of quantum mechanics. For a single particle with mass m moving in a potential V, we postulate in this formulation the following correspondence between observables and operators:

Physical observable	mathematical operator
x, y, z	$\widehat{x} = x$ etc
p_x	$\widehat{p}_x = \dfrac{\hbar}{i}\dfrac{\partial}{\partial x}$
x^2	x^2
$K_x = \dfrac{p_x^2}{2m}$	$\widehat{K}_x = \dfrac{\widehat{p}_x^2}{2m} = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$
$E = \dfrac{\mathbf{p}^2}{2m} + V(\mathbf{r})$	$\widehat{H} = \dfrac{\widehat{\mathbf{p}}^2}{2m} + V(\mathbf{r}) = -\dfrac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{r})$
$\mathbf{L} = \mathbf{r} \times \mathbf{p}$	$\widehat{\mathbf{L}} = \mathbf{r} \times \widehat{\mathbf{p}} = \mathbf{r} \times \dfrac{\hbar}{i}\boldsymbol{\nabla}$
$L_z = xp_y - yp_x$	$\widehat{L}_z = x\widehat{p}_y - y\widehat{p}_x$

As demonstrated here, the recipe for finding the Hamiltonian and the momentum operator is: Express the classical observables in terms of position and momentum variables. Then replace the momentum variables with the corresponding momentum *operators.*

This recipe can be used also for more complex systems, where both the energy and other variables may be functions of several position and momentum variables; see e.g. section 2.1 in Hemmer. (For charged particles in a magnetic field, this recipe has to be modified.)

How these quantum-mechanical operators are *used* will become clear as the course proceeds. We have already seen some of them in action. In chapter 1 we saw for example that the de Broglie wave was an eigenfunction of the momentum operator $\widehat{p}_x$. and in the box example above, both $\widehat{K}_x$ and the one-dimensional variety of the Hamiltonian $\widehat{H}$ were used.

2.2.b Postulate B (The wave-function postulate)

The state of a system is described, as completely as possible, by the wave function $\Psi(q_n, t)$. The time development of the wave function (and hence of the state) is determined by the Schrödinger equation,

$$i\hbar\frac{\partial\Psi}{\partial t} = \widehat{H}\Psi, \qquad \text{(T2.13)}$$

where $\widehat{H}$ is the Hamiltonian of the system.

Thus, the Schrödinger equation plays the role as a quantum-mechanical equation of motion. This equation determines $\Psi(q_n, t)$ uniquely when $\Psi(q_n, t_0)$ is specified at some initial time t_0. Clearly both terms of this equation are linear in Ψ. The superposition principle (T2.9) follows because the Schrödinger equation is both linear and homogeneous.

The postulate above implies that the state of a system is completely specified if we know the wave function. Both in this course and elsewhere in quantum-mechanical literature it is common to call the wave function the *state* of the system. As an example we frequently express ourselves as follows: "Suppose that the system is at $t = 0$ prepared in the state $\Psi(\mathbf{r}, 0)$".

You should also note that the wave-function postulate implies that it is not possible to obtain more information about a system than that which is contained in the wave function. *How* this information is obtained from $\Psi(q_n, t)$ will be clarified as we proceed. Cf the next postulate.

2.2.c Postulate C (Expectation-value postulate)

When a large number of measurements of an observable F is made on a system which is prepared in a state $\Psi(q_1, q_2, \cdots, q_n, t)$ (before each measurement), the average $\overline{F}$ of the measured values will approach the theretical expectation value, which is postulated to be

$$\langle\, F\,\rangle_\Psi = \int \Psi^* \widehat{F}\Psi\, d\tau, \qquad \text{(T2.14)}$$

where $d\tau = dq_1 dq_2 \cdots dq_n$ and where the integration goes over the whole range of each of the variables.

(Here, we are supposing that the wave function is normalized.) An alternative to repeating the measurement a large number of times is to measure on a large number of identically prepared systems. In both cases we use to say that we are measuring on an **ensemble** of identically prepared systems (or for short: on an ensemble prepared in the state Ψ). Pay notice to the position of the operator $\widehat{F}$; in the integrand above it acts to the right, on the factor Ψ.

As an example, let the observable F be the position coordinate x. According to the postulate, the expectation value of this observable is

$$\langle\, x \,\rangle_\Psi = \int \Psi^*\, x\, \Psi d\tau = \int x|\Psi|^2 d\tau.$$

This implies that $|\Psi|^2$ is the probability density in "position space". Thus Born's probability interpretation from 1926 is contained in the above postulate.

The expectation values of the relevant physical observables are *some* of the information contained in the wave function, but not all. Thus, if we prepare for example the particle in the box in one of the stationary states $\Psi_n(x,t)$, the number

$$\langle\, x \,\rangle = \int_0^L x|\Psi_n(x,t)|^2 dx = \int_0^L x|\psi_n(x)|^2 dx = L/2$$

only tells us that the average $\overline{x}$ of the measured values will approach the expectation value when the number of measurements increases. But the wave function contains much more information than that. For $n = 1$, e.g., the theory tells us that the distribution of a large number of measured values will agree with the probability distribution $|\psi_1(x)|^2$ shown in the diagram on page 4.

If we make only one measurement of the position x, it doesn't help much to know the theoretical probability distribution. In this case, our theory only tells us that x will lie somewhere between the walls of the box. And the wave-function postulate tells us that it is not possible to obtain more information about what this single measurement will show. Thus, as we have stated before, quantum mechanics is a theory with a **statistical character**, and breaks with our conceptions obtained from *classical* mechanics, where we are used to think that the position can be predicted accurately by Newton's laws, provided that the initial conditions are specified.

> **A small exercise:** What is the expectation value $\langle\, \mathbf{r} \,\rangle$ of the position $\mathbf{r}$ (of the electron) in the ground state $\psi_1(\mathbf{r}) = C_1 e^{-r/a_0}$ (which was discussed at the end of Tillegg 1)? [Hint: The expectation value is the "point of gravity" of the probability distribution $|\psi_1(\mathbf{r})|^2$, which is spherically symmetric.]

2.2.d Postulate D **(Measurement postulate)**

> (i) The only possible result of a precise measurement of an observable F is <u>one of the eigenvalues f_n</u> of the corresponding linear operator $\widehat{F}$.
>
> (ii) Immediately after the measurement of the eigenvalue f_n, the system is in an eigenstate of $\widehat{F}$, namely, the eigenstate ψ_n corresponding to the measured eigenvalue f_n.

(T2.15)

When there is only one eigenfunction Ψ_n with the eigenvalue f_n,

$$\widehat{F}\Psi_n = f_n\Psi_n,$$

we say that this eigenvalue is **non-degenerate**. It then follows from (ii) that the state immediately after the measurement is uniquely given by Ψ_n.

Note that (i) states that the measured result must always be one of the eigenvalues. *Which* of these eigenvalues that are measured, and the probabilities of each of them, depend on the state *before* the measurement. As an example, suppose that we prepare a non-stationary box state as a superposition of the three lowest-lying stationary states:

$$\Psi(x,t) = c_1\Psi_1(x,t) + c_2\Psi_2(x,t) + c_3\Psi_3(x,t).$$

Then (as we shall soon see) a measurement of the energy can only give one of the three results E_1, E_2 or E_3. If the result is for example E_2, the system will according to (ii) be left in the state Ψ_2 after the measurement. Here we see that the measurement *changes the state* of the system. That a measurement changes the state of the system in this way, is in fact more of a rule than an exception in quantum physics.

A new measurement of the energy (after the first measurement with the result E_2) will again give the result E_2, and will thus according to (ii) *not* change the state. *This* is the exception.

2.3 Hermitian and non-hermitian operators, commutators, etc

2.3.a Real expectation values demand hermitian operators

The operator $\widehat{F}$ representing a measurable quantity (an obsevable) F must be **hermitian**. This is a mathematical property which ensures that the eigenvalues (which are possible measurement results) are real, and also that the expectation values are real. Taking the latter property as our starting point, we must require that

$$\langle F \rangle^* = \langle F \rangle, \qquad \text{that is,} \qquad \int \Psi(\widehat{F}\Psi)^* d\tau = \int \Psi^* \widehat{F}\Psi d\tau.$$

This should hold for all normalizable (square integrable) wave functions Ψ. In section 2.2, Hemmer shows that this is equivalent to requiring that

$$\int (\widehat{F}\Psi_1)^*\Psi_2 d\tau = \int \Psi_1^*\widehat{F}\Psi_2 d\tau, \tag{T2.16}$$

for all square-integrable functions Ψ_1 and Ψ_2. When this condition is satisfied, we say that the operator $\widehat{F}$ is per definition hermitian. Note that the operator $\widehat{F}$ acts on Ψ_1 on the left side of (T2.16) and on Ψ_2 on the right side. If it is possible by mathematical manipulations to move the operator from the former position to the latter, it then follows that it is hermitian. We shall soon se that all the operators listed on page 8 have this property, and that this implies that their eigenvalues are real. Yoe should memorize (T2.16), because it will turn out to be very useful on many occations.

2.3.b The adjoint, $\widehat{F}^\dagger$, of the operator $\widehat{F}$

In order to be able to distinguish between hermitian and non-hermitian operators, we must take the trouble to learn what is meant by the **adjoint**, $\widehat{A}^\dagger$ (expressed as "A-dagger"), of an operator $\widehat{A}$. This mathematical object is defined by the equation

$$\int (\widehat{A}\Psi_1)^*\Psi_2 d\tau \overset{\text{def}}{=} \int \Psi_1^* \widehat{A}^\dagger \Psi_2 d\tau, \quad \forall \quad (\text{ square-integrable})\ \Psi_1 \text{ and } \Psi_2. \tag{T2.17}$$

To understand the meaning of this definition, we can go straight to an example: The adjoint of the operator $\widehat{A} = \partial/\partial x$, that is, $(\partial/\partial x)^\dagger$, is defined by

$$\int \left(\frac{\partial}{\partial x}\Psi_1\right)^* \Psi_2 d\tau \overset{\text{def}}{=} \int \Psi_1^* \left(\frac{\partial}{\partial x}\right)^\dagger \Psi_2 d\tau$$

Ahem.. Well, how do we *find* this adoint, $(\partial/\partial x)^\dagger$? Answer: By taking the expression on the left as our starting point, and manipulating mathematically in such a way that we end up with differentiation of Ψ_2 instead of Ψ_1. The result of these manipulations will be an operator acting on Ψ_2, and this operator is per definition the adjoint of $\partial/\partial x$. In this case, the necessary manipulations are essentially limited to a partial integration:

$$\int_{-\infty}^{\infty} (\frac{\partial}{\partial x}\Psi_1)^*\Psi_2 dx = \left[\Psi_1^*\Psi_2\right]_{x=-\infty}^{x=\infty} - \int_{-\infty}^{\infty} \Psi_1^* \frac{\partial}{\partial x}\Psi_2 dx.$$

Here, the boundary term is equal to zero, because square-integrable functions must be zero in the limit $x \to \pm\infty$. If our position space contains more variables (y and z in addition to x), we can readily integrate also over y and z in the equation above, and thus we obtain the general result:

$$\int (\frac{\partial}{\partial x}\Psi_1)^*\Psi_2 d\tau = \int \Psi_1^*(-\frac{\partial}{\partial x})\Psi_2 d\tau \overset{\text{def}}{=} \int \Psi_1^* \left(\frac{\partial}{\partial x}\right)^\dagger \Psi_2 d\tau.$$

Thus, from the definition it follows that the adjoint of the operatoren $\partial/\partial x$ is

$$\left(\frac{\partial}{\partial x}\right)^\dagger = -\frac{\partial}{\partial x}.$$

This example should illustrate that *the adjoint is in general not the same as complex conjugation.* We also see that the operator $\partial/\partial x$ is *not* hermitian. This is because for a hermitian operator $\widehat{F}$, the result $\widehat{F}^\dagger$ of the manipulations must be identical to $\widehat{F}$ according to (T2.16). We then say that $\widehat{F}$ is **self-adjoint**:

$$\widehat{F}^\dagger = \widehat{F} \qquad \text{(self-adjoint=hermitian)}.$$

It is now a simple matter to check the hermiticity of our usual operators. The observable x is represented by the operator $\widehat{x} = x$ (multiplication by x), the potential energy is represented by the operator $V(x)$, etc. It is easy to see that both of these are hermitian. To be slightly more general, let us consider multiplication by a complex function $g(x)$ (or a complex constant c). We have

$$\int [g(x)\Psi_1]^*\Psi_2 d\tau = \int \Psi_1^*\, g^*(x)\, \Psi_2 d\tau,$$

that is,

$$[g(x)]^\dagger = g^*(x), \quad \text{and}$$
$$c^\dagger = c^* \qquad (c \text{ a complex constant}).$$

(So in *this* case the adjoint is is the same as the complex conjugate). Since x and $V(x)$ are real, it then follows that

$$x^\dagger = x^* = x,$$
$$[V(x)]^\dagger = V(x) \qquad \text{(the potential energy)},$$

To proceed, let $\widehat{A}$ and $\widehat{B}$ be two general operators. From the definition of the adjoint we then have

$$\int [\widehat{A}(\widehat{B}\Psi_1)]^*\Psi_2 d\tau = \int (\widehat{B}\Psi_1)^*(\widehat{A}^\dagger\Psi_2)d\tau = \int \Psi_1^*\widehat{B}^\dagger\widehat{A}^\dagger\Psi_2 d\tau \overset{\text{def}}{=} \int \Psi_1^*(\widehat{A}\widehat{B})^\dagger\Psi_2 d\tau, \quad \text{(T2.18)}$$

leading to the simple rule

$$(\widehat{A}\widehat{B})^\dagger = \widehat{B}^\dagger\widehat{A}^\dagger. \quad \text{(T2.19)}$$

Using this rule, you can easily find the adjoint of a product of three operators, and so on. Note that the *order* of operators is in general important. (The exception is when they **commute**, meaning that their order is *not* important.) This rule can be used e.g. to show that the momentum operators (and multipla of these) are hermitian:

$$\widehat{p}_x^\dagger = (\frac{\hbar}{i}\frac{\partial}{\partial x})^\dagger = (\frac{\partial}{\partial x})^\dagger(\frac{\hbar}{i})^\dagger = -\frac{\partial}{\partial x}(\frac{\hbar}{-i}) = \frac{\hbar}{i}\frac{\partial}{\partial x} = \widehat{p}_x,$$
$$(\widehat{p}_x\widehat{p}_x)^\dagger = \widehat{p}_x^\dagger\widehat{p}_x^\dagger = \widehat{p}_x\widehat{p}_x, \quad \text{etc.}$$

Furthermore, it is easy to see that

$$(\widehat{A}+\widehat{B})^\dagger = \widehat{A}^\dagger + \widehat{B}^\dagger,$$

and then it is not difficult to see that also the Hamiltonian is hermitian, as we must of course require for the operator representing the observable $E = K + V$:

$$\widehat{H}^\dagger = \left[\frac{\widehat{p}_x^2}{2m} + V(x)\right]^\dagger = \widehat{H}.$$

A little exercise:

a1. How fast must $|f(x)|$ approach zero when $|x| \to \infty$, if we want the function $f(x)$ to be sqare integrable (and hence normalizable in the usual sense), so that the integral $\int_{-\infty}^{\infty}|f(x)|^2dx$ *exists*?

a2. By a partial integration it can be shown that

$$\int \left(\frac{1}{i}\frac{\partial f}{\partial y}\right)^* g\, d^3x = \int f^*\,\frac{1}{i}\frac{\partial g}{\partial y}\, d^3x$$

for all square-integrable complex functions $f(x,y,z)$ and $g(x,y,z)$. What is then the adjoint of the operator $\frac{1}{i}\frac{\partial}{\partial y}$? [Hint: Check the definition of the adjoint on page 12.]

b. Show that the Laplace operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

is hermitian. [Hint: Use the formula $(\widehat{A}\widehat{B})^\dagger = \widehat{B}^\dagger\widehat{A}^\dagger$ to find $(\frac{\partial}{\partial x}\frac{\partial}{\partial x})^\dagger$.]
c1. Show that the operator $x\widehat{p}_x$ is non-hermitian.
c2. Show that the operator $\frac{1}{2}(x\widehat{p}_x + \widehat{p}_x x)$ is hermitian.

2.3.c A little bit about commutators

As already mentioned, the order of operators is in general important, except when they commute, that is, when their **commutator** is equal to zero. As you can see page 25 in Hemmer or in section 3.3 in B&J, it is easy to show that

$$(x\widehat{p}_x - \widehat{p}_x x)F(x,y,z) \equiv [x,\widehat{p}_x]F(x,y,z) = i\hbar\, F(x,y,z)$$

for for an arbitrary function F. The **operator identitety**

$$x\widehat{p}_x - \widehat{p}_x x \equiv [x,\widehat{p}_x] = i\hbar, \tag{T2.20}$$

or more generally,

$$[x_k,\widehat{p}_l] = i\hbar\,\delta_{kl},$$

play central roles in quantum mechanics. In section 5.4 in B&J, it is shown how the commutator $[x,\widehat{p}_x] = i\hbar$ can be used to prove **Heisenberg's uncertainty relation**,

$$\boxed{(\Delta x)_\psi(\Delta p_x)_\psi \geq \tfrac{1}{2}\hbar, \qquad \forall \quad \text{square-integrable} \quad \psi.} \tag{T2.21}$$

The "moral" is that when the operators $\widehat{A}$ and $\widehat{B}$ (corresponding to the observables A and B) do not commute, then the two observables can not have sharp values simultaneously. This uncertainty relation can be generalized to

$$\boxed{(\Delta A)(\Delta B) \geq \tfrac{1}{2}\left|\left\langle\, i[\widehat{A},\widehat{B}]\,\right\rangle\right|,} \quad \text{(generalized uncertainty relation).} \tag{T2.22}$$

Some simple rules of calculation for commutators:

$$\begin{aligned}[\widehat{A}+\widehat{B},\widehat{C}+\widehat{D}] &= (\widehat{A}+\widehat{B})(\widehat{C}+\widehat{D}) - (\widehat{C}+\widehat{D})(\widehat{A}+\widehat{B}) \\ &= [\widehat{A},\widehat{C}] + [\widehat{A},\widehat{D}] + [\widehat{B},\widehat{C}] + [\widehat{B},\widehat{D}];\end{aligned} \tag{T2.23}$$

$$\begin{aligned}[\widehat{A},\widehat{B}\widehat{C}] &= [\widehat{A},\widehat{B}]\widehat{C} + \widehat{B}[\widehat{A},\widehat{C}] \\ [\widehat{A}\widehat{B},\widehat{C}] &= \widehat{A}[\widehat{B},\widehat{C}] + [\widehat{A},\widehat{C}]\widehat{B}.\end{aligned} \tag{T2.24}$$

The last two relations are easiest to check calculating backwards. It is also easy to show Jakobi's identity:

$$[\widehat{A},[\widehat{B},\widehat{C}]] + [\widehat{B},[\widehat{C},\widehat{A}]] + [\widehat{C},[\widehat{A},\widehat{B}]] = 0. \tag{T2.25}$$

Example 1

In order to check whether the angular-momentum operator $\widehat{L}_z = x\widehat{p}_y - y\widehat{p}_x$ is hermitian, we can calculate its adjoint. Since x and $\widehat{p}_y$ are hermitian and commute, we find that $\widehat{L}_z$ is self-adjoint,

$$\widehat{L}_z^\dagger = (x\widehat{p}_y - y\widehat{p}_x)^\dagger = \widehat{p}_y^\dagger x^\dagger - \widehat{p}_x^\dagger y^\dagger = \widehat{p}_y x - \widehat{p}_x y = x\widehat{p}_y - y\widehat{p}_x = \widehat{L}_z,$$

that is, hermitian, as we must demand for an operator representing a physical observable.

Example 2

Using (T2.23) we can calculate the commutator between $\widehat{L}_x$ and $\widehat{L}_y$:

$$\begin{aligned}[\widehat{L}_x, \widehat{L}_y] &= [y\widehat{p}_z - z\widehat{p}_y, z\widehat{p}_x - x\widehat{p}_z] \\ &= [y\widehat{p}_z, z\widehat{p}_x] - [z\widehat{p}_y, z\widehat{p}_x] - [y\widehat{p}_z, x\widehat{p}_z] + [z\widehat{p}_y, x\widehat{p}_z].\end{aligned}$$

In the first commutator on the right, both y and $\widehat{p}_x$ commute with z (and with each other). This way we find that

$$[y\widehat{p}_z, z\widehat{p}_x] = y\widehat{p}_z z\widehat{p}_x - z\widehat{p}_x y\widehat{p}_z = y\widehat{p}_x(\widehat{p}_z z - z\widehat{p}_z) = y\widehat{p}_x[\widehat{p}_z, z] = -i\hbar\, y\widehat{p}_x,$$

and furthermore that

$$\begin{aligned}[z\widehat{p}_y, z\widehat{p}_x] &= 0, \\ [y\widehat{p}_z, x\widehat{p}_z] &= 0, \\ [z\widehat{p}_y, x\widehat{p}_z] &= i\hbar\, x\widehat{p}_y.\end{aligned}$$

In this manner we arrive at the so-called **angular-momentum algebra**:

$$\begin{aligned}&[\widehat{L}_x, \widehat{L}_y] = i\hbar\widehat{L}_z, \\ &[\widehat{L}_y, \widehat{L}_z] = i\hbar\, \widehat{L}_x, \\ &[\widehat{L}_z, \widehat{L}_x] = i\hbar\, \widehat{L}_y.\end{aligned} \tag{T2.26}$$

Using these relations, it is easy to show that

$$[\widehat{L}_x^2, \widehat{L}_z] = \widehat{L}_x[\widehat{L}_x, \widehat{L}_z] + [\widehat{L}_x, \widehat{L}_z]\widehat{L}_x = \widehat{L}_x(-i\hbar\widehat{L}_y) + (-i\hbar\widehat{L}_y)\widehat{L}_x,$$

and similarly that

$$[\widehat{L}_y^2, \widehat{L}_z] = \widehat{L}_y(i\hbar\widehat{L}_x) + (i\hbar\widehat{L}_x)\widehat{L}_y,$$

while the commutator $[\widehat{L}_z^2, \widehat{L}_z]$ is of course equal to zero. Altogether this gives

$$[\widehat{\mathbf{L}}^2, \widehat{L}_z] = [\widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2, \widehat{L}_z] = 0, \quad \text{q.e.d.} \tag{T2.27}$$

As we shall see later, this means that it is possible to find simultaneous eigenfunctions of the operators $\widehat{\mathbf{L}}^2$ and e.g. $\widehat{L}_z$. In such a state, the uncertainties of both observables $\mathbf{L}^2$ and L_z are equal to zero. The "moral" is that the *size* ($|\mathbf{L}|$) of the angular momentum $\mathbf{L}$ for a particle can have a sharp value together with one of its components, e.g. L_z.

On the other hand it follows from the angular-momentum algebra (T2.10) and the generalized uncertainty relation,

$$(\Delta F)_\Psi(\Delta G)_\Psi \geq \tfrac{1}{2}\left|\left\langle i[\widehat{F},\widehat{G}]\right\rangle_\Psi\right| \qquad \forall \text{ (square-integrable) } \Psi,$$

that the measurable components L_x, L_y and L_z of the angular momentum vector $\mathbf{L}$ of the particle can *not* have sharp values simultaneously (because the operators do not commute). This breaks with our classical-mechanical conceptions. Take for example the angular momentum of the earth with respect to the sun, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, which has both a well-defined size and a well-defined direction (normal to the orbital plane). For the electron in the hydrogen atom, this is not possible.

2.4 Eigenfunctions and eigenvalues

2.4.a The spectrum of an operator

We have already seen that the mathematical concepts **eigenfunction** and **eigenvalue** play important roles in quantum mechanics. Hemmer gives in his section 2.4.1 a very concise exposition of the central aspects, and a similar discussion can be found in sections 5.1–4 in B&J, which you should study closely. Some comments :

1. In section 2.1 above we found that the **spectrum** (the possible eigenvalues) of the Hamiltonian for the one-dimensional box is

$$\left\{ E_n = \frac{\hbar^2\pi^2}{2mL^2}\,n^2 \;\middle|\; n = 1, 2, 3, \cdots \right\}.$$

We also found that the eigenfunctions corresponding to this **discrete** energy spectrum are normalizable (to 1).

2. In an exercise we have already encountered the Hamiltonian

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \tfrac{1}{2}m\omega^2x^2$$

of the one-dimensional harmonisc oscillator and two of its eigenfunctions with the corresponding eigenvalues:

$$\psi_0(x) = C_0 e^{-m\omega x^2/2\hbar} \quad (\text{with } E_0 = \tfrac{1}{2}\hbar\omega) \qquad \text{and} \qquad \psi_1(x) = C_1 x\, e^{-m\omega x^2/2\hbar} \quad (\text{with } E_1 = \tfrac{3}{2}\hbar\omega).$$

We shall later see that these describe respectively the ground state and the first excited state of the oscillator, and that the complete spectrum is

$$\left\{ E_n = \hbar\omega(n + \tfrac{1}{2}) \;\middle|\; n = 0, 1, 2, \cdots \right\}. \qquad \text{(T2.28)}$$

It turns out that all the corresponding eigenfunctions contain the same exponential factor $\exp(-m\omega x^2/2\hbar)$, multiplied by a polynomial of degree n. These eigenfunctions therefore all approach zero (more or less quickly) as $x \to \pm\infty$. Thus they are all normalizable to 1. This property, of normalizability for bound-state wave functions, turns out to be general:

Eigenfunctions corresponding to discrete eigenvalues can always be normalized to 1. (T2.29)

What happens if we try to solve the time-independent Schrödinger equationfor the oscillator, $\widehat{H}\Psi = E\psi$, for an energy E which is not equal to any of the eigenvalues $E_n = \hbar\omega(n+\frac{1}{2})$? The answer is that the "solution" becomes infinite as $|x|$ approaches infinity. Such "solutions" do not qualify as eigenfunctions, neither from a mathematical viewpoint nor from a physical one:

$$\boxed{\text{Only solutions of the eigenvalue equation which are normalizable (in a certain sense) are counted as eigenfunctions.}} \qquad \text{(T2.30)}$$

3. As an example of an operator with a *continuous* eigenvalue spectrum, we may consider the momentum operator $\widehat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$. The eigenvalue equation then is

$$\widehat{p}_x\psi_p = p\psi_p, \qquad \text{or} \quad \frac{d\psi}{dx} = \frac{ip}{\hbar}\,\psi_p$$

(where other possible variables like y, z, t are kept fixed). Here, p is the eigenvalue. This equation can be integrated:

$$\frac{d\psi_p}{\psi_p} = \frac{ip}{\hbar}\,dx \qquad \Longrightarrow \qquad \ln\psi_p = \ln C + \frac{ipx}{\hbar} \qquad \Longrightarrow \qquad \psi_p(x) = Ce^{ipx/\hbar}.$$

(We have in fact seen this momentum eigenfunction before, in the discussion of the de Broglie waves in Tillegg 1.) In this solution, the eigenvalue p can take any real value $p \in (-\infty, +\infty)$. Complex eigenvalues are excluded, because they will make $|\psi(x)|^2$ infinite either when x goes to $+\infty$ or $-\infty$. This is not acceptable for an eigenfunction. Thus we can conclude that the momentum operator has a continuous real spectrum, from $-\infty$ to $+\infty$.

However, even for a real eigenvalue p the eigenfunction is not normalizable to 1; the integral $\int_{-\infty}^{\infty}|\psi_p(x)|^2dx$ does not exist, because $|\psi_p(x)|^2 = |C|^2$ is constant for all x. Later we shall see that in this case we must use a different kind of "normalization", the so-called delta-function normalization. (This is the reason for the reservation "in a certain sense" in (T2.30).)

> We should also note that the momentum eigenfunction $\psi_p(x) = Ce^{ipx/\hbar}$ — and the corresponding de Broglie wave $\Psi_p(x,t) = Ce^{i(px-Et)/\hbar}$ (with $E = p^2/2m$) — describes a particle with *completely well-defined* (sharp) momentum $\mathbf{p} = p\hat{\mathbf{e}}_x$. This wave function extends over an infinite space, and therefor must be an idealization. A *real physical* state must somehow be limited to a finite space and be normalizable to 1. Then it can not have a completely sharp wave number. This means that the momentum $\mathbf{p} = \hbar\mathbf{k}$ of a *real physical* state must always be uncertain, at least to a small extent, seen from a mathematical viewpoint.

4. As discussed in Tillegg 1 (and in an exercise) the Hamiltonian for an electron (with charge $-e$) moving in an electrostatic potential $U(r) = e/(4\pi\epsilon_0 r)$ is

$$\widehat{H} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0 r}.$$

It turns out that this operator, which essentaily describes the hydrogen atom, for $E < 0$ has a *discrete* spectrum,

$$E_n = -\tfrac{1}{2}\alpha^2\frac{mc^2}{n^2}, \qquad n = 1, 2, \cdots.$$

For $n = 1$ we have already found the corresponding energy eigenfunction, $\psi = (\pi a_0^3)^{-1/2} e^{-r/a_0}$. Both this ground state and the eigenfunctions belonging to the other discrete energy levels are normalizable to 1 (square integrable), and describe bound states, in agreement with (T2.29). We can also say that these states are **localized**, in the sense that they approach zero more or less quickly for large r.

For $E > 0$ the energy is not quantized; we have a *continuous* spectrum extending from $E = 0$ upwards. Thus, the Hamiltonian of this system has a **mixed spectrum**. The energy eigenfunctions belonging to the continuous part of the spectrum are *not localized*; they extend over an infinite space (like the momentum eigenfunctions) and are not normalizable to 1. For such unbound states one must again use delta-function normalization. In general, it turns out that

For eigenfunctions corresponding to a continuopus (part of a) spectrum, one must use delta-function normalization. (T2.31)

2.4.b Eigenvalues as measured values

As explained in section 5.2 in B&J,

(i) The eigenvalues f_n of a hermitian operator $\widehat{F}$ are real, and

(ii) in the corresponding eigenstate Ψ_n, the observable F with certainty has the value f_n. (T2.32)

Comments:

(i) According to the measurement postulate, a measurement of $F = f_n$ will leave the system in the corresponding eigenstate, given by

$$\widehat{F}\Psi_n = f_n \Psi_n,$$

where we remember that $\widehat{F}$ is hermitian, and therefore has real eigenvalues. We assume that Ψ_n is normalized. The (real) expectation value of F then is equal to the eigenvalue:

$$\langle F \rangle_{\Psi_n} = \int \Psi_n^* \widehat{F} \Psi_n d\tau = \int \Psi_n^* f_n \Psi_n d\tau = f_n \int \Psi_n^* \Psi_n d\tau = f_n.$$

Thus the eigenvalue f_n is real, and that is a relief (!), when we remember that this eigenvalue is in fact a possible measurement result.

(ii) A new measurement of F (immediately after the first one, which left the system in the state Ψ_n) will with certainty give $F = f_n$ once more. We can therefore state that in the state Ψ_n the observable F has the sharp value f_n. To prove this, we only have to show that the **uncertainty** (the root-mean-square deviation from the expectation value f_n) is equal to zero:

$$(\Delta F)^2_{\Psi_n} \equiv \left\langle (F - \langle F \rangle_{\Psi_n})^2 \right\rangle_{\Psi_n} = \left\langle (F - f_n)^2 \right\rangle_{\Psi_n} = \int \Psi_n^* (\widehat{F} - f_n)^2 \Psi_n d\tau = 0, \quad \text{q.e.d.} \tag{T2.33}$$

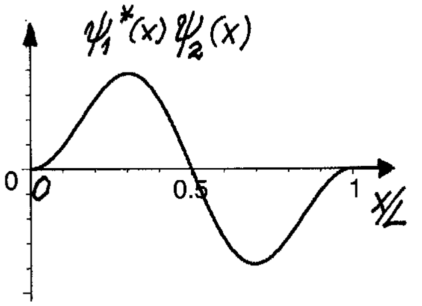
Here we have used the eigenvalue equation $(\widehat{F} - f_n)\Psi_n = 0$.

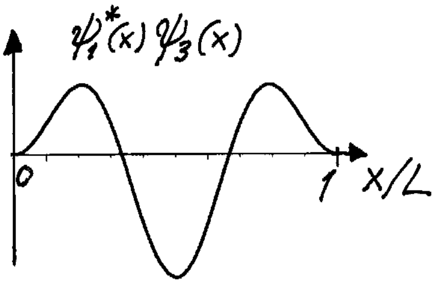
2.4.c Orthogonality

An important rule, which will be used frequently in this course, is the following:

Two eigenfunctions Ψ_n and Ψ_m of a hermitian operator are **orthogonal** if the eigenvalues f_n and f_m are different. With this we mean that:

$$f_m \neq f_n \qquad \Longrightarrow \qquad \int \Psi_m^* \Psi_n d\tau = 0. \tag{T2.34}$$





The figure shows the eigenfunction *products* $\psi_1^*(x)\psi_2(x)$ and $\psi_1^*(x)\psi_3(x)$ for a particle in a box. The product on the left is antisymmetric with respect to the midpoint (because ψ_1 is symmetric and ψ_2 is antisymmetric), and then the orthogonality follows because we have an antysymmetric integrand. The product on the right, on the other hand, gives a symmetric integrand. In this case it takes a bit of calculation to show that the integral is actually equal to zero. However, such explicit calculations are completely unnecessary. As you can see in section 2.4.3 in Hemmer, or in 5.3 in B&J, it is straightforward to prove the general rule above:

With $\widehat{F}\Psi_n = f_n\Psi_n$ and $\widehat{F}\Psi_k = f_k\Psi_k$, it follows from the relation

$$\int (\widehat{F}\Psi_n)^*\Psi_k d\tau = \int \Psi_n^* \widehat{F}\Psi_k d\tau,$$

valid for the hermiteian operator $\widehat{F}$, that

$$0 = \int (\widehat{F}\Psi_n)^*\Psi_k d\tau - \int \Psi_n^* \widehat{F}\Psi_k d\tau = (f_n - f_k)\int \Psi_n^*\Psi_k d\tau, \quad \text{q.e.d.}$$

2.4.d Orthogonalization using a "*Complete set of commuting operators*"***[2]

As we all know, it happens that one or more eigenvalues are **degenerate**, meaning that there is more than one eigenfunction having the same eigenvalue f_n. An example is the first excited energy level of the hydrogen atom, $E_2 = -\frac{1}{2}\alpha^2 mc^2/4$: The number of independent eigenfunctions for this level is four; we then say that the (degree of) **degeneracy** is 4.

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[2] Sections marked by *** are not compulsory in FY1006/TFY4215. The present section can well be skipped till after the treatment of the hydrogen atom.

Now, these four wave functions, ψ_1, ψ_2, ψ_3, ψ_4, need not be orthogonal, even if they are independent. At least, the rule (T2.34) does not ensure orthogonality in this case. In such a case we would like to construct an orthogonal set, because as we shall see it is an advantage with orthogonality. One way to achieve this is to use the so-called **Gram-Schmidt orthogonalization procedure**, which will be discussed later.

Another way is to work with simultaneous eigenfunctions of a so-called **complete set of commuting operators**. The hydrogen atom is well suited to illustrate this method. The degeneracy of the hydrogen levels is partly due to the spherical symmetry of this problem. From this symmetry it follows that the Hamiltonian $\widehat{H}$ commutes with the angular-momentum operator $\widehat{\mathbf{L}}$ and with the square $\widehat{\mathbf{L}}^2$ of this operator. At the same time the components of $\widehat{\mathbf{L}}$ commute with $\widehat{\mathbf{L}}^2$, but not with each other, as we have seen above. This means that the operator set $\widehat{H}$, $\widehat{\mathbf{L}}^2$ and $\widehat{L}_z$ commute with each other. Then (as we shall see in chapter 4) there exists a simultaneous set of eigenfunctions of these three operators. The bound states (for $E < 0$) are the well-known eigenfunction set

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi),$$

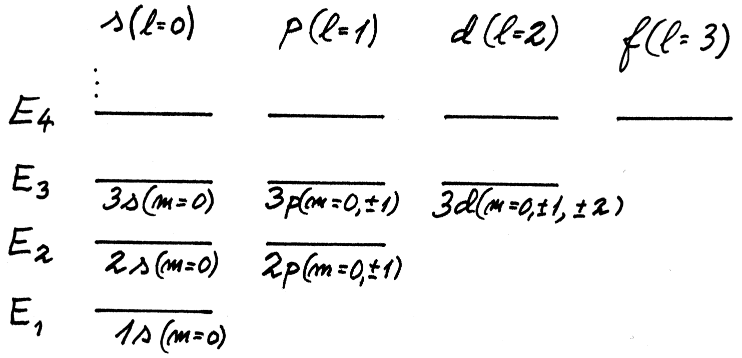
which satisfy the eigenvalue equations

$$\left\{\begin{array}{c} \widehat{H} \\ \widehat{\mathbf{L}}^2 \\ \widehat{L}_z \end{array}\right\}\psi_{nlm} = \left\{\begin{array}{c} E_n \\ \hbar^2 l(l+1) \\ \hbar m \end{array}\right\}\psi_{nlm}, \qquad \begin{array}{l} n = 1,2,3,\cdots, \\ l = 0,1,2,,\cdots,n-1, \\ m = 0,\pm 1,\cdots,\pm l. \end{array}$$

Here we note that the energy is independent of the magnetic quantum number m, which for a given angular-momentum quantum number l can take the values $m = 0,\pm 1,\cdots,\pm l$, altogether $2l+1$ values. This is the so-called m degeneracy, which is common for all spherically symmetric potentials. Furthermore, the energy is also independent of l, which for a given principal quantum number n can take the values $l = 0,1,2,\cdots,n-1$. This is the so-called l degeneracy, which is characteristic for the $1/r$ potential.[3] The total (degree of) degeneracy for the energy level E_n then becomes

$$g_n = \sum_{l=0}^{n-1} 2l+1 = 1 + (2\cdot 1+1) + (2\cdot 2+1) + \cdots + (2\cdot(n-1)+1) = \tfrac{1}{2}n(1+2n-1) = n^2,$$

which is 4 for $n = 2$, 9 for $n = 3$, etc. The energy levels and the corresponding states can be illustrated by the following level scheme:



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[3] The $1/r$ form of the potential actually corresponds to a "hidden" symmetry, which causes the l degeneracy.

You should note that all these states are orthogonal. This is because there is only one eigenfunction ψ_{nlm} for each combination nlm of quantum numbers, and then it follows from (T2.34) that we have an orthogonal set. More specifically, we can state that the ground state ψ_{100} is orthogonal to all the excited states because the energy eigenvalues are different. The same holds for any two states with different energies, as e.g. for the pair ψ_{200} and ψ_{300} and for the pair ψ_{210} and ψ_{310}.

But what about eigenfunctions belonging to the same energy level, like e.g. the $2s$ state ψ_{200} and the $2p$ states ψ_{21m}, with $m = 0, \pm 1$? The answer is that ψ_{200} is orthogonal to the states ψ_{21m} because the eigenvalues of $\widehat{\mathbf{L}}^2$ are different (respectively 0 and $2\hbar^2$). Similarly, the three states ψ_{211}, ψ_{210} and ψ_{21-1} are orthogonal because they are eigenfunctions of $\widehat{L}_z$ with different eigenvalues (respectively $\hbar$, 0, and $-\hbar$).

The "moral" is that the orthogonality of the n^2 energy eigenfunctions with energy E_n is ensured by the fact that they are simultaneous egenfunctions of $\widehat{H}$ and a suitable additional set of operators (here $\widehat{\mathbf{L}}^2$ and $\widehat{L}_z$). If this set is chosen in such a way that there is only one eigenfunction for each combination of eigenvalues, orthogonality is ensured by (T2.34). We then say that this set of operators (here $\widehat{H}$, $\widehat{\mathbf{L}}^2$ and $\widehat{L}_z$) constitute a **complete set of commuting operators**. Another choice of operators (e.g. $\widehat{H}$, $\widehat{\mathbf{L}}^2$ and $\widehat{L}_x$) can also be a complete set of commuting operators. The simultaneous eigenfunctions of *this* set will be linear combinations of the original set of eigenfunctions. ("Moral": The g_n eigenfunctions with energy E_n are not unique.) Note also that the set $\widehat{H}$ and $\widehat{\mathbf{L}}^2$ are *not* a complete set of commuting operators.

A small challenge: (1) Find a complete set of commuting operators for the three-dimensional harmonic oscillator (with $V = \frac{1}{2}m\omega^2 r^2$). (2) Same for a two-dimensional quadratic box.

2.4.e Wave functions (and other functions) as "vectors"

(Griffiths, ch. 3 and Appendix)

The notation

$$\int \Psi_n^* \Psi_m d\tau \equiv \langle\, \Psi_n, \Psi_m \,\rangle$$

is used because the integral on the left is called the **scalar product** of the two functions Ψ_n and Ψ_m. The notions "scalar product" and "orthogonality" are borrowed from the theory of (abstract) vector spaces. Wave functions describing physically realizable states must must be normalizable to 1, that is, they must belong to the class of complex, square-integrable functions. These functions satisfy all the criteria which define an abstract **vector space**:

- The sum of two such (square integrable) functions is itself a (square integrable) function
- Addition of functions is commutative and associative $[f + g = g + f;\quad (f + g) + h = f + (g + h)]$
- There exists a "null-function", $f \equiv 0$
- Multiplication by a compleks constant gives a new function

etc. The list actually is a bit longer, but the message is already clear. The complex square-integrable functions belong to a complex vector space, denoted by $\mathrm{L}_2(-\infty, \infty) \equiv \mathrm{L}_2$ in mathematics, and called a Hilbert space in physics. The dimension of this space is infinite, because there are infinitely many linearly independent functions of this kind. [4]

As scalar product (also called the **inner product**) of two complex functions f and g we use

$$\langle\, f, g\,\rangle \equiv \int f^* g d\tau. \tag{T2.35}$$

This is analoguous to the scalar productet of two ordinary (complex) vectors (which you have possibly not used?), which in the physics literature is defined by

$$\langle\, \mathbf{a}, \mathbf{b}\,\rangle \equiv \mathbf{a}^* \cdot \mathbf{b} \equiv a_x^* b_x + a_y^* b_y + a_z^* b_z \tag{T2.36}$$

With this *definition* the scalar product is linear in the *second* factor: When c is a complex number, it follows from (T2.35) that[5]

$$\langle\, f, cg\,\rangle = c\,\langle\, f, g\,\rangle\,, \qquad \text{while} \qquad \langle\, cf, g\,\rangle = c^*\,\langle\, f, g\,\rangle\,.$$

Note that the scalar product is in general a complex number, and that

$$\langle\, f, g\,\rangle^* = \langle\, g, f\,\rangle\,.$$

The **length** $|\mathbf{a}|$ of an ordinary complex vector $\mathbf{a}$ is defined as the root of the scalar product $\langle\, \mathbf{a}, \mathbf{a}\,\rangle$, so that

$$|\mathbf{a}|^2 = \langle\, \mathbf{a}, \mathbf{a}\,\rangle = \mathbf{a}^* \cdot \mathbf{a} = |a_x|^2 + |a_y|^2 + |a_z|^2.$$

In a similar manner, we define the length $||f||$, also called the **norm**, of the "vector" f such that

$$||f||^2 = \langle\, f, f\,\rangle = \int f^* f d\tau. \tag{T2.37}$$

The norm of a normalized wave function Ψ thus is $||\Psi|| = 1$. Given another function $\tilde{\psi}$ which is *not* normalized, we can construct a normalized version ψ as follows:

$$\psi = \frac{\tilde{\psi}}{||\psi||} = \frac{\tilde{\psi}}{\sqrt{\langle\, \tilde{\psi}, \tilde{\psi}\,\rangle}}.$$

This is analoguous to $\hat{\mathbf{a}} = \mathbf{a}/|\mathbf{a}|$ being a unit vector.

A small exercise:
Find the norm $||e^{-x^2/2}||$ of the function $e^{-x^2/2}$, where x goes from $-\infty$ to $+\infty$.

Another exercise:
1. What are the scalar products $\langle\, \hat{\mathbf{e}}_x, \mathbf{a}\,\rangle$ and $\langle\, \hat{\mathbf{e}}_y, \mathbf{a}\,\rangle$ for the vector $\mathbf{a} = 3\hat{\mathbf{e}}_x + 2\hat{\mathbf{e}}_y$?
2. Let $\mathbf{b} = 3\hat{\mathbf{e}}_x + 4i\hat{\mathbf{e}}_y$ be a complex vector. What are $\langle\, \mathbf{b}, \mathbf{b}\,\rangle$, $\langle\, \mathbf{a}, \mathbf{b}\,\rangle$ and $\langle\, \mathbf{b}, \mathbf{a}\,\rangle$? [Hint: Cf (T2.36). Answer: 25, $9 + 8i$ and $9 - 8i$.]
3. What is the length of $\mathbf{b}$? [Answer: $||\mathbf{b}|| \equiv |\mathbf{b}| = \sqrt{\langle\, \mathbf{b}, \mathbf{b}\,\rangle} = \sqrt{\mathbf{b}^* \cdot \mathbf{b}} = 5$.]

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[4] That the number of linearly independent square-integrable complex functions is infinite, can be understood e.g. by considering the energy eigenfunctions $\psi_n(x)$ of the harmonic oscillator as an example. We have one such eigenfunction for each of the infinite number of eigenvalues, $E_n = \hbar\omega(n + \frac{1}{2})$. All these functions are orthogonal and hence linearly independent according to (T2.34).

[5] One can just as well define the inner product in such a way that it is linear in the first factor. This is commonly done in the mathematical literature. However, in quantum mechanics we use the definition above: In the integral $\langle\, f, g\,\rangle$, the first factor is f^*.

2.4.f The delta function and δ-function normalization

Dirac's δ function

Dirac's δ function is discussed in Appendix B in Hemmer's book, and in Appendix A in B&J. Here we summarize some of the most important properties. The δ "function" is defined by the property

$$\int_{-\infty}^{\infty} f(x)\delta(x)dx = f(0) \tag{T2.38}$$

for all functions which are continuous at the origin. The definition implies that $\delta(x)$ must be equal to zero for all $x \neq 0$ and infinitely large for $x = 0$, in such a way that

$$\int_{-\infty}^{\infty} \delta(x)dx = 1. \tag{T2.39}$$

By introducing $x' = -x$ as a new integration variable we understand that the function is even,

$$\delta(-x) = \delta(x). \tag{T2.40}$$

Introducing $x' = |a|x$ in the integral $\int f(x)\delta(ax)dx$, we see that

$$\delta(ax) = \delta(|a|x) = \frac{1}{|a|}\,\delta(x). \tag{T2.41}$$

Other important properties are [6]

$$\begin{aligned} \int_{a-\Delta}^{a+\Delta} f(x)\delta(x-a)dx &= f(a), && \text{(T2.42)}\\ f(x)\delta(x-a) &= f(a)\delta(x-a), && \text{(T2.43)}\\ x\delta(x-a) &= a\delta(x-a). && \text{(T2.44)} \end{aligned}$$

The δ function is not a function in the strict sense of the word, but a so-called **generalized function**. We can consider it as the limit of a **sequence** of ordinary functions $\delta_\epsilon(x)$,

$$\delta(x) = \lim_{\epsilon\longrightarrow 0} \delta_\epsilon(x), \tag{T2.45}$$

where the width of the graph of $\delta_\epsilon(x)$ approaches zero, while the area under the graph is equal to 1 the whole time. There of course exist many such sequences. A simple example is a rectangular area of width ϵ and height $1/\epsilon$:

$$\delta(x) = \lim_{\epsilon\longrightarrow 0} \delta_\epsilon(x) = \lim_{\epsilon\longrightarrow 0} \left\{ \begin{array}{lll} 1/\epsilon & \text{for} & |x| \leq \epsilon/2, \\ 0 & \text{for} & |x| > \epsilon/2. \end{array} \right. \tag{T2.46}$$

This is called a **representation** of the δ function. In this and other representations, it goes without saying that the limit should be taken *after* the calculation of the integrals:

$$\lim_{\epsilon\longrightarrow 0} \int_{-\infty}^{\infty} f(x)\delta_\epsilon(x)dx = f(0). \tag{T2.47}$$

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[6] Note that it is sufficient to integrate over a small interval containing the point where the δ function is different from zero, which is the point where the argument is zero.

It is easy to see that this condition is satisfied by (T2.46). Hemmer and B&J give several examples of such representations which all have this property. Here we shall focus in particular on two, where the functions $\delta_\epsilon(x)$ are respectively

$$\delta_\epsilon(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx-\epsilon|k|}dk = \frac{\epsilon}{\pi(x^2+\epsilon^2)}$$

and

$$\delta_\epsilon(x) = \frac{1}{2\pi}\int_{-1/\epsilon}^{1/\epsilon} e^{ikx}dk = \frac{\sin(x/\epsilon)}{\pi x}.$$

The areas under these curves are both equal to 1, and the "widths" approach zero as $\epsilon \longrightarrow 0$, while the heights become infinite. The advantage of these two representations is that we can in fact allow ourselves to take the limit $\epsilon \longrightarrow 0$ *before* the integration. Thus we set

$$\boxed{\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}dk = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikx}dk.} \qquad \text{(T2.48)}$$

We can call this a Fourier representation of the δ function, because it has the form of a Fourier integral. Here, you may be frightened by the fact that this integral in fact does not exist. However, it turns out that we may still work with this representation. In the end our results will be correct.

A small exercise: Which δ function is represented by the integral

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ik(x-a)}dk\ ?$$

3 dimensions

In three dimensions the defining equation (T2.38) is replaced by

$$\int\int\int f(\mathbf{r})\delta(\mathbf{r})d^3r = f(\mathbf{0}).$$

This is satisfied by

$$\delta(\mathbf{r}) = \delta(x)\delta(y)\delta(z).$$

The charge density of a point particle with charge q placed at the point $\mathbf{r} = \mathbf{a}$ is proportional to such a δ function:

$$\rho(\mathbf{r}) = q\delta(\mathbf{r}-\mathbf{a}).$$

This illustrates in a concrete way what a three-dimensional δ function is.

δ-function normalization

We have already mentioned in (T2.3) that one must use δ-function "normalization" for eigenfunctions corresponding to a continuous part of a spectrum. As an example we may consider the momentum eigenfunctions $\psi_p(x) = Ce^{ipx/\hbar}$. Since $|\psi_p(x)|^2 = |C|^2$, the normalization integral clearly diverges. The momentum eigenfunctionen therefore is not normalizable in the usual meaning of the word.

What about orthogonality? Let us choose $C = (2\pi\hbar)^{-1/2}$ and calculate the scalar product of ψ_p and $\psi_{p'}$,

$$\langle\, \psi_p, \psi_{p'} \,\rangle \equiv \int_{-\infty}^{\infty} \psi_p^*(x)\psi_{p'}(x)dx = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ipx/\hbar}e^{ip'x/\hbar}d(x/\hbar) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i(p'-p)y}dy.$$

Here we have introduced $y = x/\hbar$ as a new integration variable. Comparing with (T2.48) we see that the result is

$$\boxed{\langle\, \psi_p, \psi_{p'} \,\rangle \equiv \int_{-\infty}^{\infty} \psi_p^*(x)\psi_{p'}(x)dx = \delta(p'-p).} \qquad \left(\begin{array}{c}\delta\text{-function}\\ \text{normalization}\end{array}\right) \qquad \text{(T2.49)}$$

With the above choice of normalization constant,

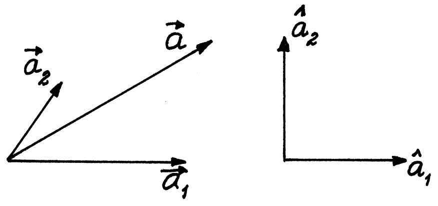
$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}\, e^{ipx/\hbar}$$

we thus get a scalar product between $\psi_p(x)$ and $\psi_{p'}(x)$ which simply is $\delta(p'-p) = \delta(p-p')$. This is called δ-function normalization (although the function is not normalizable in the proper sense).

2.5 Expansion in eigenfunctions **(Cf 2.5 in Hemmer, 3.7 in B&J)**

2.5.a The notion of a "complete set" (or basis)

We have just seen that square-integrable functions are vectors in an infinite-dimensional vector space. Also the term **basis** (or **comlete set**) is borrowed from the theory of vector spaces. Let us illustrate this by considering an ordinary two-dimensional vector space.



Here, the arbitrary vector **a** may very well be expanded in a basis consisting of the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, which are two arbitrary, linearly independent vectors. However, it is much more practical to an *orthonormalized* basis set $\hat{\mathbf{a}}_1$ and $\hat{\mathbf{a}}_2$,

$$\langle\, \hat{\mathbf{a}}_i, \hat{\mathbf{a}}_j \,\rangle = \delta_{ij}, \qquad i, j = 1, 2. \qquad \text{(T2.50)}$$

The unit vectors $\hat{\mathbf{a}}_1$ and $\hat{\mathbf{a}}_2$ are constructed as linear combinations of the two independent vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, using the following recipe:

$$\hat{\mathbf{a}}_1 = \frac{\mathbf{a}_1}{|\mathbf{a}_1|}, \qquad \hat{\mathbf{a}}_2 = \frac{\mathbf{a}_2 - \langle\, \hat{\mathbf{a}}_1, \mathbf{a}_2 \,\rangle\, \hat{\mathbf{a}}_1}{|\mathbf{a}_2 - \langle\, \hat{\mathbf{a}}_1, \mathbf{a}_2 \,\rangle\, \hat{\mathbf{a}}_1|}.$$

Note that $\langle\, \hat{\mathbf{a}}_1, \mathbf{a}_2 \,\rangle\, \hat{\mathbf{a}}_1$ is the component of $\mathbf{a}_2$ along $\hat{\mathbf{a}}_1$. The numerator in the last expression therefore is the component of $\mathbf{a}_2$ *normal* to $\hat{\mathbf{a}}_1$. The denominator takes care of the normalization. This recipe can also be used to orthogonalize *functions*, and is then called the **Gram–Schmidt-orthogonalization** procedure:

A small exercise: Suppose that $\tilde{\psi}_1$, $\tilde{\psi}_2$ and $\tilde{\psi}_3$ are three linearly independent (but not necessarily normalized and orthogonal) functions. From these functions we can construct three orthonormalized linear combinations. One way of doing this is as follows:

$$\psi_1 = \frac{\tilde{\psi}_1}{||\tilde{\psi}_1||}, \quad \psi_2 = \frac{\tilde{\psi}_2 - \left\langle \psi_1, \tilde{\psi}_2 \right\rangle \psi_1}{||\tilde{\psi}_2 - \left\langle \psi_1, \tilde{\psi}_2 \right\rangle \psi_1||}, \quad \psi_3 = \frac{\tilde{\psi}_3 - \left\langle \psi_1, \tilde{\psi}_3 \right\rangle \psi_1 - \left\langle \psi_2, \tilde{\psi}_3 \right\rangle \psi_2}{||\tilde{\psi}_3 - \left\langle \psi_1, \tilde{\psi}_3 \right\rangle \psi_1 - \left\langle \psi_2, \tilde{\psi}_3 \right\rangle \psi_2||}.$$

Thes are obviously normalized. Check that they are also orthogonal:

$$\langle \psi_1, \psi_2 \rangle = 0 = \langle \psi_1, \psi_3 \rangle = \langle \psi_2, \psi_3 \rangle \,.$$

With the basis (T2.50), the expansion formula for the arbitrary vector **a** is

$$\mathbf{a} = a_1\hat{\mathbf{a}}_1 + a_2\hat{\mathbf{a}}_2 = \sum_{i=1}^{2} a_i\hat{\mathbf{a}}_i. \tag{T2.51}$$

The advantage of the orthonormalized basis becomes more clear when we calculate the **projections** of the vector **a** onto the two basis vectors:

$$\langle \hat{\mathbf{a}}_1, \mathbf{a} \rangle = \langle \hat{\mathbf{a}}_1, a_1\hat{\mathbf{a}}_1 + a_2\hat{\mathbf{a}}_2 \rangle = a_1,$$

$$\langle \hat{\mathbf{a}}_2, \mathbf{a} \rangle = \langle \hat{\mathbf{a}}_2, a_1\hat{\mathbf{a}}_1 + a_2\hat{\mathbf{a}}_2 \rangle = a_2,$$

or in one sweep:

$$\underline{\langle \hat{\mathbf{a}}_i, \mathbf{a} \rangle} = \left\langle \hat{\mathbf{a}}_i, \sum_j a_j\hat{\mathbf{a}}_j \right\rangle = \sum_j a_j \langle \hat{\mathbf{a}}_i, \hat{\mathbf{a}}_j \rangle = \sum_j a_j\delta_{ij} = \underline{a_i}, \qquad i = 1, 2. \tag{T2.52}$$

Thus, the expansion coefficients a_1 and a_2 simply are equal to the *projections* of the vector **a** onto the respective basis vectors.

By inserting the coefficients we thus find that the arbitrary vector **a** can be expanded as:

$$\mathbf{a} = \langle \hat{\mathbf{a}}_1, \mathbf{a} \rangle \hat{\mathbf{a}}_1 + \langle \hat{\mathbf{a}}_2, \mathbf{a} \rangle \hat{\mathbf{a}}_2 = \sum_i \langle \hat{\mathbf{a}}_i, \mathbf{a} \rangle \, \hat{\mathbf{a}}_i. \tag{T2.53}$$

All this is of course completely trivial, but it is included here because exactly the same tecqnique can be used for functions, as we shall see below.

2.5.b Complete sets of *functions*

As explained in Hemmer and in 3.7 in B&J (and in section 2.4.d above), we can consider normalized wave functions as vectors in an infinite-dimensional complex vector space. A basis for this space must therefore contain an infinite number of functions.

Strangely enough, it turns out that the eigenfunction sets of our hermitian operators all are **complete sets of functions** or bases. An example of such a hermitian operator is the Hamiltonian of the one-dimensional oscillator,

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \tfrac{1}{2}m\omega^2x^2.$$

As stated above (although still not proved) this operator has the discrete and non-degenerate spectrum

$$E_n = \hbar\omega(n + \tfrac{1}{2}), \qquad n = 0, 1, 2, \cdots .$$

We shall later see that each of the corresponding orthonormalized eigenfunctions,

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n\left(x\sqrt{m\omega/\hbar}\right) e^{-m\omega x^2/2\hbar} \qquad (\langle\, \psi_k, \psi_n \,\rangle = \delta_{kn}), \tag{T2.54}$$

goes as a **Hermite polynomial** H_n (of degree n) in the dimensionless variable $x\sqrt{m\omega/\hbar} \equiv \xi$, multiplied by the Gauss function $\exp(-m\omega x^2/2\hbar) \equiv \exp(-\xi^2/2)$ (which guarantees normalizability). Note that there is an infinite number of these functions.

It can be proved mathematically that this set of functions is complete. With this we mean that an arbitrary square-integrable function $g(x)$ can be *expanded* in this set,

$$g(x) = \sum_{n=0}^{\infty} c_n \psi_n(x). \tag{T2.55}$$

This expansion is analoguous to the expansion of the vector $\mathbf{a}$ in terms of the two unit vectors $\hat{\mathbf{a}}_1$ and $\hat{\mathbf{a}}_2$. Thus, in the formula above the normalized eigenfunction $\psi_n(x)$ plys the role of a "unit vector".

In analogy with the preceeding section, the *orthonormality* of these "unit vectors" makes it easy to determine the expansion coefficients c_n. These simply are the projections of the function $g(x)$ onto the respective "unit vectors" $\psi_n(x)$,

$$c_n = \langle\, \psi_n, g \,\rangle \equiv \int_{-\infty}^{\infty} \psi_n^*(x) g(x) dx, \tag{T2.56}$$

in analogy with $a_i = \langle\, \hat{\mathbf{a}}_i, \mathbf{a} \,\rangle$. To remove any doubts, let us *calculate* these projections. The projection of $g(x)$ onto $\psi_n(x)$ is

$$\langle\, \psi_n, g \,\rangle = \left\langle\, \psi_n, \sum_k c_k \psi_k \,\right\rangle = \sum_k c_k \,\langle\, \psi_n, \psi_k \,\rangle = \sum_k c_k \delta_{nk} = c_n, \quad \text{q.e.d.} \tag{T2.57}$$

In analogy with the formula $\mathbf{a} = \sum_i a_i \hat{\mathbf{a}}_i = \sum_i \langle\, \hat{\mathbf{a}}_i, \mathbf{a} \,\rangle\, \hat{\mathbf{a}}_i$, we thus get the following expansion formula for the arbitrary function $g(x)$:

$$g(x) = \sum_n c_n \psi_n(x) = \sum_n \langle\, \psi_n, g \,\rangle\; \psi_n(x). \tag{T2.58}$$

Expansion formula $\Longrightarrow$ completeness relation

The fact that the arbitrary function $g(x)$ can be expanded in this way, implies that the basis set of eigenfunctions $\psi_n(x)$ has a special property; they satisfy the so-called **completeness relation**. This is easily shown by rewriting the formula above slightly: By writing out the scalar product as an explicit integral (with the integration variable x') and interchanging the order of summation and integration we find that

$$g(x) = \sum_n \left(\int_{-\infty}^{\infty} \psi_n^*(x') g(x') dx'\right) \psi_n(x) = \int_{-\infty}^{\infty} \left(\sum_n \psi_n(x)\psi_n^*(x')\right) g(x') dx'. \tag{T2.59}$$

This may be compared with the relation (cf (T2.42))

$$g(x) = \int_{-\infty}^{\infty} \delta(x - x')g(x')dx'. \tag{T2.60}$$

Since these relations hold for all continuous (and square-integrable) functions $g(x)$, the two formulae can only be consistent if the set of eigenfunctions satisfy the so-called **completeness relation**:

$$\boxed{\sum_n \psi_n(x)\psi_n^*(x') = \delta(x - x').} \tag{T2.61}$$

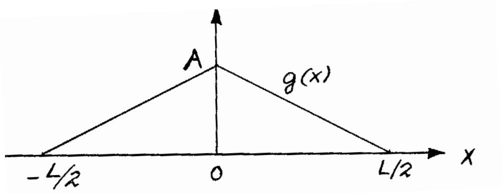
Completeness relation $\Longrightarrow$ expansion formula

We have just derived the completeness relation from the expansion formula. But it is also possible to go the opposite way: By replacing the δ function in the identity (T2.60) by the left side of (T2.61), we find that the expansion formula follows from the completeness relation:

$$\begin{aligned} g(x) &= \int_{-\infty}^{\infty} \delta(x - x')\, g(x')\, dx' = \int_{-\infty}^{\infty} \left(\sum_n \psi_n(x)\psi_n^*(x')\right) g(x')\, dx' \\ &= \sum_n \left(\int_{-\infty}^{\infty} \psi_n^*(x')g(x')dx'\right) \psi_n(x) \\ &\equiv \sum_n \langle\, \psi_n, g\,\rangle\; \psi_n(x) \equiv \sum_n c_n\psi_n(x). \end{aligned} \tag{T2.62}$$

Thus the expansion formula and the completeness relation are completely equivalent.

For the oscillator eigenfunctions, the completeness can as mentioned be proved. Such proofs exist also for the eigenfunctions of many of the other hermitian operators used in quantum mechanics, but not for all. For a hermitian operator for which a proof has not been established, it is customary in quantum mechanics to *assume* that the set of its eigenfunctions is complete. This can be regarded as another postulate.



A small exercise: Assume that we have a one-dimensional box potential, equal to zero for $|x| < \frac{1}{2}L$ and infinite for $|x| > \frac{1}{2}L$. The energy eigenfunctions for this potential can (for $|x| < \frac{1}{2}L$) be written on the form

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{L}}\cos(n\pi x/L) & \text{for} \quad n = 1, 3, 5, \cdots, \\ \sqrt{\frac{2}{L}}\sin(n\pi x/L) & \text{for} \quad n = 2, 4, 6, \cdots. \end{cases}$$

The figure shows a function $g(x)$ which is equal to zero for $|x| > \frac{1}{2}L$ and equal to $A(\frac{1}{2}L - |x|)$ for $|x| < \frac{1}{2}L$. Why are the coefficients c_2, c_4, c_6 etc in the expansion formula $g(x) = \sum_{n=1}^{\infty} c_n\psi_n(x)$ all equal to zero?

In section 2.5.1 in Hemmer you can see that the formalism is essentially the same for all complete sets corresponding to discrete spectra. For eigenfunction sets corresponding to *continuous* spectra, you can see in Hemmer that the formalism is *almost* the same; one only replaces the sums in the expansion formula and in the completeness relation by integrals (over the continuous spectrum).

Here, we shall consider one example, namely the eigenfunction set of the momentum operator $\widehat{p}_x$. As an alternative to the procedure in Hemmer's 2.5.1, we start by proving the completeness relation, and then use this to derive the expansion formula (cf the discussion above).

2.5.c Momentum eigenfunctions as a basis. Fourier integrals

We have seen that the momentum operator $\widehat{p}_x = (\hbar/i)\partial/\partial x$ is hermitian, with a continuous spectrum $p \in (-\infty, \infty)$. In this case it is easy to *show* that the eigenfunctions

$$\psi_p(x) = (2\pi\hbar)^{-1/2} e^{ipx/\hbar}, \tag{T2.63}$$

with the delta-function normalization

$$\int_{-\infty}^{\infty} \psi_p^*(x)\psi_{p'}(x)dx = \delta(p-p'), \tag{T2.64}$$

constitute a complete set. In this case we must expect that both the completeness relation and the expansion formula contain *integrals* over the contiunuous set of eigenvalues p (instead of sums over discrete eigenvalues). Thus we *expect* to find a completeness relation of the form

$$\int_{-\infty}^{\infty} \psi_p(x)\psi_p^*(x')dp = \delta(x-x'), \tag{T2.65}$$

and an expansion formula

$$g(x) = \int_{-\infty}^{\infty} \phi(p)\, \psi_p(x)\, dp, \tag{T2.66}$$

where the function $\phi(p)$ plays the role of "expansion coefficient".

Proof: We start by proving the completeness relation (T2.65), by inserting the momentum eigenfunctions (T2.63) on the left side of (T2.65), getting as expected:

$$\int_{-\infty}^{\infty} \psi_p(x)\psi_p^*(x')dp = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i(x-x')(p/\hbar)} d(p/\hbar) = \delta(x-x'), \quad \text{q.e.d.}$$

Then we apply this relation on the right side of the identity (T2.60), in analogy with the procedure in (T2.62):

$$\begin{aligned} g(x) &= \int_{-\infty}^{\infty} \delta(x-x')g(x')dx' = \int_{-\infty}^{\infty} dx' \left(\int_{-\infty}^{\infty} dp\, \psi_p(x)\psi_p^*(x')\right) g(x') \\ &= \int_{-\infty}^{\infty} dp \left(\int_{-\infty}^{\infty} dx'\, \psi_p^*(x')g(x')\right) \psi_p(x) \\ &\equiv \int_{-\infty}^{\infty} dp\, \langle\, \psi_p, g\, \rangle\; \psi_p(x) \equiv \int_{-\infty}^{\infty} dp\, \phi(p)\, \psi_p(x), \quad \text{q.e.d.} \end{aligned} \tag{T2.67}$$

This expansion formula,

$$\boxed{g(x) = \int_{-\infty}^{\infty} \phi(p)\, \psi_p(x)\, dp,} \tag{T2.68}$$

is known as a **Fourier integral**. We note that the "expansion coefficient" $\phi(p)$ also in this case is the projection of the function $g(x)$ (which we want to expand) onto the "unit vector", which here is $\psi_p(x)$:

$$\boxed{\phi(p) = \langle\, \psi_p, g \,\rangle = \int_{-\infty}^{\infty} \psi_p^*(x)\, g(x)\, dx.} \tag{T2.69}$$

This expression is known as the **Fourier transform** of the function $g(x)$. These formulae for the Fourier integral and the Fourier transform differ from those in Appendix A.2 in B&J, or page 383 in Hemmer,

$$\begin{aligned} g(x) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} G(k)\, e^{ikx}\, dk, \\ G(k) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ikx}\, g(x)\, dx, \end{aligned} \tag{T2.70}$$

only by the notation. (See also Griffiths page 46.)

A sufficient (but possibly not necessary) condition for the existence of the Fourier transform $\phi(p)$ (or if you like, $G(k)$) is that the Fourier integral converges absolutely, meaning that the integral

$$\int_{-\infty}^{\infty} |f(x)| dx$$

exists (is finite). This condition is more restrictive than that of square integrability (which ensures normalizability). When the former condition is satisfied, we are free to interchange the order integrations (and summations), as we have done above. Under these conditions, it turns out that the Fourier transform has the same normalization as the function $g(x)$:

$$\int_{-\infty}^{\infty} |g(x)|^2 dx = \int_{-\infty}^{\infty} |\phi(p)|^2 dp. \tag{T2.71}$$

This is known as **Parceval's relation**.

While the discrete set of oscillator eigenfunctions (T2.54) are normalizable to 1 and belong to the "vector space of square-integrable functions" (Hilbert space), you should note that this is not the case for the momentum eigenfunctions

$$\psi_p(x) \;\propto\; e^{ipx/\hbar} \equiv e^{ikx}.$$

As we have seen, these are not normalizable to 1, and require delta-function "normalization". Thus they do not belong to the Hilbert space. It is somewhat peculiar that these functions, which do not themselves belong to the Hilbert space, form an excellent *basis* for this space. But this is of course well known by those who have a little experience with Fourier integrals: It is perfectly alright to use a basis outside the space as long as this basis is complete.

3 dimensions

The above formalism is easily generalized to 2 or 3 dimensions. Thus the complete set of eigenfunctions of the momentum operator $\widehat{\mathbf{p}} = \frac{\hbar}{i}\boldsymbol{\nabla}$ is the plane-wave set

$$\psi_{\mathbf{p}}(\mathbf{r}) = (2\pi\hbar)^{-3/2}\, e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} = \psi_{p_x}(x)\psi_{p_y}(y)\psi_{p_z}(z). \tag{T2.72}$$

This set satisfies the completeness relation

$$\int \psi_{\mathbf{p}}(\mathbf{r})\,\psi^*_{\mathbf{p}}(\mathbf{r}')\,d^3p = \delta(\mathbf{r}-\mathbf{r}'), \tag{T2.73}$$

and constitutes a basis for the three-dimensional Fourier integral: An arbitrary square-integrable function $g(\mathbf{r})$ can be expanded as

$$\boxed{g(\mathbf{r}) = \int \phi(\mathbf{p})\,\psi_{\mathbf{p}}(\mathbf{r})d^3p,} \tag{T2.74}$$

and the Fourier transform is the projection of the function $g(\mathbf{r})$ onto the the "vector" $\psi_{\mathbf{p}}(\mathbf{r})$,

$$\boxed{\phi(\mathbf{p}) = \langle\,\psi_{\mathbf{p}}, g\,\rangle = \int \psi^*_{\mathbf{p}}(\mathbf{r})\,g(\mathbf{r})\,d^3r.} \tag{T2.75}$$

It should be noticed that also other complete sets can be used. As a special example we can mention the eigenfunctions of the hydrogen atom (cf the Coulomb problem), with

$$\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0\,r}.$$

In this case only the bound states are square integrable, while the unbound states require delta-function normalization. In such a case, both the expansion formula and the completeness relation will contain a sum (over discrete eigenvalues) *and* an integral (over continuous eigenvalues). Thus you should note that the bound states alone do not constitute a complete set. See e.g. B&J, section 5.3.

A small exercise: The Gauss function

$$g(x) = (2\pi\sigma^2)^{-1/4}e^{-x^2/4\sigma^2}$$

can be written as a Fourier integral,

$$g(x) = \int_{-\infty}^{\infty} \phi(p)\,\psi_p(x)\,dp, \qquad \text{with} \quad \psi_p(x) = (2\pi\hbar)^{-1/2}e^{ipx/\hbar}. \tag{1}$$

Show that the Fourier transform of $g(x)$, $\phi(p) = \int_{-\infty}^{\infty}\psi_p^*(x)g(x)dx$, is given by

$$\phi(p) = \left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4} e^{-\sigma^2p^2/\hbar^2}.$$

As a check, you can insert this result into (1) to see if you are able to reproduce the original function $g(x)$. Given:

$$\int_{-\infty}^{\infty} e^{-ax^2+bx}dx = \sqrt{\pi/a}\,e^{b^2/4a} \qquad (\Re\mathrm{e}(a) > 0).$$

2.5.d Physical interpretation of the expansion coefficients

(cf 2.5.2 in Hemmer, 3.8 in B&J)

Fourier analysis, based on the completeness of the momentum eigenfunctions, is an important tool in many physical disciplines and also in technology. But why is the completeness of the eigenfunction sets of all the other hermitian operators so important in quantum mechanics?

Much of the answer lies in the **physical interpretation of the expansion coefficients**. This is beautifully explained in Hemmer's section 2.5.2 and in section 3.8 in B&J. Here follows another variation over the same theme:

Suppose that we have prepared a physical system, or really an ensemble of such systems, in a state Ψ. And suppose that we measure some observable F for this ensemble. (This could for example be the energy E). We also assume that the corresponding hermitian operator $\widehat{F}$ has a discrete, non-degenerate [7] spectrum $\{f_n\}$ with a corresponding orthonormalized set of eigenfunctions ψ_n:

$$\widehat{F}\psi_n = f_n\psi_n \; ; \qquad \langle\, \psi_k, \psi_n \,\rangle \equiv \int \psi_k^* \psi_n \, d\tau = \delta_{kn}. \tag{T2.76}$$

We can of course expand the state Ψ of the system in this complete set of states ψ_n:

$$\Psi = \sum_n c_n \psi_n \; ; \qquad c_n = \langle\, \psi_n, \Psi \,\rangle \equiv \int \psi_n^* \, \Psi \, d\tau. \tag{T2.77}$$

Let us insert this expansion into the formula for the expectation value of the observable F. Using (T2.16) we get:

$$\begin{aligned}\langle\, F \,\rangle_\Psi &= \int \Psi^* \, \widehat{F} \, \Psi \, d\tau = \int (\widehat{F}\Psi)^* \Psi \, d\tau \\ &= \int \left(\widehat{F} \sum_n c_n \psi_n \right)^* \Psi \, d\tau = \int \left(\sum_n c_n \widehat{F} \psi_n \right)^* \Psi \, d\tau \\ &= \sum_n c_n^* f_n^* \underbrace{\int \psi_n^* \, \Psi \, d\tau}_{c_n} \qquad (f_n \text{ reell}) \\ &= \sum_n c_n^* f_n c_n = \sum_n |c_n|^2 f_n. \end{aligned} \tag{T2.78}$$

Here we must now remember the measurement postulate, which tells us that each measurement of F must give one of the eigenvalues f_n and and leave the system in the corresponding eigenstate ψ_n. According to ordinary probability theory, the expectation value can therefore also be expressed as follows:

$$\langle\, F \,\rangle_\Psi = \sum_n P_n f_n, \tag{T2.79}$$

where P_n is the probability of measuring the eigenvalue f_n. By comparing the two formulae above (which are valid for any state Ψ), we can state that the probability must be the square of the expansion coefficient:

$$P_n = |c_n|^2.$$

---

[7] An eigenvalue is **non-degenerate** when there is only one eigenfunction with this eigenvalue.

The "moral" that can be extracted from this argument is the following physical interpretation of the expansion coefficients in (T2.56):

> When the system is in the state Ψ, the probability that a measurement of F gives the eigenvalue f_n (and leaves the system in the state ψ_n) is
>
> $$P_n = |c_n|^2 = |\langle\, \psi_n, \Psi\, \rangle|^2 \equiv \left| \int \psi_n^* \Psi \, d\tau \right|^2 . \tag{T2.80}$$

For this reason, the expansion coefficient c_n itself is often called the **probability amplitude** of measuring f_n (and leaving the system in the corresponding eigenstate ψ_n). Here, it is important to note that this amplitude simply is the projection of the state Ψ of the system *before* the measurement onto the resulting state ψ_n *after* the measurement;

$$c_n = \langle\, \psi_n, \Psi\, \rangle \, .$$

This is a very important rule in quantum mechanics. Note that a measurement normally *changes* the state of the system. This is more of a rule than an exception. An example is when we measure the energy of a system and get one of the possible results E_n, leaving the system in the corresponding energy eigenstate ψ_n. If the system was in a different state before the measurement, its state has been changed by the measurement. Note that a new measurement of the energy after the measurement of E_n will give the same value. This second measurement therefore does *not* change the state. (So this is the exception.)

Note also that the sum of the probabilities is equal to 1:

$$\sum_n P_n = \sum_n |c_n^2| = 1.$$

This is in fact the normalization condition for the state Ψ. (Cf equation (T2.11)).

> **A small exercise:** A harmonic oscillator is prepared in a state described by the wave function
>
> $$\psi(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega(x-a)^2/2\hbar},$$
>
> that is, in a wave function with same *form* as the ground state of the oscillator, only displaced a distance a compared to this state. What is the probability that a measurement of the energy of this oscillator gives the ground-state energy $E_0 = \frac{1}{2}\hbar\omega$? What is the state of the oscillator after a measurement of the ground-state energy? Check that the values obtained for the probability for $a = 0$ and for $a \to \infty$ are reasonable (Given: The integral page 31.)

A simple example

Let our system be a particle in a box, with the energy eigenfunctions $\psi_n(x) = \sqrt{2/L}\, \sin(n\pi x/L)$ and the energy eigenvalues $E_n = n^2 E_1$; $E_1 = \hbar^2\pi^2/(2mL^2)$; $n = 1, 2, \cdots$. Then we know that

$$\Psi_n(x,t) = \psi_n(x)\, e^{-iE_n t/\hbar}$$

are (stationary) solutions of the Schrödinger equation for the box,

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t}=\widehat{H}\Psi(x,t).$$

According to the superposition principle, any linear combination of these stationary states will satisfy the Schrödinger equation and describe acceptable physical states for the particle in the box. As an example of such a linear combination, describing a non-stationary state, we consider the wave function

$$\Psi(x,t)=\tfrac{1}{2}\sqrt{3}\,e^{-iE_1t/\hbar}\,\psi_1(x)+\tfrac{1}{2}\,e^{-iE_2t/\hbar}\,\psi_2(x).$$

In this case, only two probability amplitudes differ from zero. These are

$$c_1=\tfrac{1}{2}\sqrt{3}\,e^{-iE_1t/\hbar}\qquad\text{and}\qquad c_2=\tfrac{1}{2}\,e^{-iE_2t/\hbar}.$$

We note that the sum of the two probabilities is

$$\sum_n|c_n|^2=|c_1|^2+|c_2|^2=\tfrac{3}{4}+\tfrac{1}{4}=1,$$

corresponding to Ψ being normalized. (Try to check that Ψ is normalized.) When the system is prepared in this state Ψ, a measurement of the energy will return the ground-state energy E_1 (and leave the system in the ground state) with probability 3/4, while the probability of measuring the energy $E_2(=4E_1)$ and and leaving the system in the first excited state is 1/4. The expectation value of the energy is

$$\langle\,E\,\rangle_\Psi=\sum_n|c_n|^2E_n=\frac{3}{4}\,E_1+\frac{1}{4}\cdot4E_1=\frac{7}{4}\,E_1.$$

If you like, you may calculate the uncertainty of the energy, by first finding the expectation value of E^2.

2.5.e Measurement of a degenerate eigenvalue ***[8]

In cases where the measured eigenvalue is degenerate, we must be a little bit more specific, both in the formulation of the measurement postulate, and in the pysical interpretation of the expansion coefficients.

As an example, we consider a three-dimensional isotropic harmonic oscillator [with $V=\frac{1}{2}m\omega^2r^2=\frac{1}{2}m\omega^2x^2+\frac{1}{2}m\omega^2y^2+\frac{1}{2}m\omega^2z^2$.] By writing the energy eigenfunctions as products of one-dimensional oscillator eigenfunctions (one for each of the three directions x, y and z), it is easy to see that the energy levels are

$$E_N=\hbar\omega(N+3/2),\qquad N=0,1,2,\cdots. \tag{T2.81}$$

(See page 83 in Hemmer or section 7.1 in B&J.) For $N\geq1$ we find that these levels are degenerate, with a (degree of) degeneracy

$$g_N=\tfrac{1}{2}(N+1)(N+2). \tag{T2.82}$$

---

[8] Sections marked *** are not compulsory in Fy1006/TFT4215.

Thus for a given energy quantum number N there are g_N energy eigenstates with the same energy E_N,

$$\psi_{Ni}, \quad i = 1, 2, \cdots, g_N.$$

Altogether these states form a complete set, in which we may expand an arbitrary square-integrable function $g(\mathbf{r})$, including the state Ψ which we have prepared for the oscillator:

$$\Psi = \sum_{N=0}^{\infty} \sum_{i=1}^{g_N} c_{Ni}\psi_{Ni} = c_{01}\psi_{01} + \sum_{i=1}^{3} c_{1i}\psi_{1i} + \sum_{i=1}^{6} c_{2i}\psi_{2i} + \cdots . \tag{T2.83}$$

The expansion coefficients are the projections

$$c_{Ni} = \langle\, \psi_{Ni}, \Psi \,\rangle \equiv \int_{-\infty}^{\infty} \psi_{Ni}^* \, \Psi \, d^3r. \tag{T2.84}$$

A series of measurements of the energy of the oscillator (when it is in the state Ψ) will give an average close to the theoretical expectation value. This expectation value can be expressed in terms of the expansion coefficients, as in (T2.78):

$$\begin{aligned}
\langle\, E \,\rangle_\Psi &= \int \left(\widehat{H}\Psi\right)^* \Psi \, d^3r \\
&= \int \left(\sum_N \sum_i c_{Ni} \widehat{H} \psi_{Ni} \right)^* \Psi \, d^3r \\
&= \sum_N \sum_i c_{Ni}^* E_N \underbrace{\int \psi_{Ni}^* \, \Psi \, d^3r}_{c_{Ni}} \\
&= \sum_N \left(\sum_{i=1}^{g_N} |c_{Ni}|^2 \right) E_N .
\end{aligned} \tag{T2.85}$$

On the other hand we know that

$$\langle\, E \,\rangle_\Psi = \sum_N P_N E_N, \tag{T2.86}$$

where P_N is the probability of measuring the energy E_N. Comparing, we see that the probability of measuring the degenerate energy eigenvalue E_N is

$$P_N = \sum_{i=1}^{g_N} |c_{Ni}|^2. \tag{T2.87}$$

Immediately after this measurement of the energy E_N the oscillator will be in a state described by the (normalized) wave function

$$\psi_N \equiv \frac{\sum_{i=1}^{g_N} c_{Ni}\psi_{Ni}}{||\sum_{i=1}^{g_N} c_{Ni}\psi_{Ni}||}. \tag{T2.88}$$

Here we see that the part of the wave function Ψ which is "not compatible with the energy E_N is peeled off" by this measurement. This shows how the measurement postulate must be formulated when an eigenvalue is degenerate. For the non-degenerate ground state ($N = 0$) you can note that the state after the measurement of E_0 according to this formula becomes

$$\frac{c_{01}\psi_{01}}{||c_{01}\psi_{01}||} = \frac{c_{01}}{|c_{01}|}\,\psi_{01},$$

in agreement with the formulation page 23. (The phase factor $c_{01}/|c_{01}|$ is of no importance.)

2.5.f Physical interpretation in the continuous case

The physical interpretation of the expansion coefficients in the continuous case is described in a very clear and concise way page 33–34 in Hemmer. (Sea also Griffiths page 106–107 and B&J page 208.)

Here we again consider the example with the momentum eigenfunctions,

$$\psi_p(x) = (2\pi\hbar)^{-1/2} e^{ipx/\hbar}, \qquad \widehat{p}_x\psi_p(x) = p\psi_p(x), \qquad p \in (-\infty, \infty). \tag{T2.89}$$

Instead of an arbitrary function $g(x)$, we now choose to expand the time-dependent wave function $\Psi(x,t)$ of a one-dimensional quantum-mechanical system:

$$\Psi(x,t) = \int_{-\infty}^{\infty} \Phi(p,t)\,\psi_p(x)\,dp. \tag{T2.90}$$

Since $\Psi(x,t)$ depends on time, the Fourier transform $\Phi(p,t)$ will also be time dependent:

$$\Phi(p,t) = \langle\, \psi_p, \Psi(t)\,\rangle \equiv \int_{-\infty}^{\infty} \psi_p^*(x)\,\Psi(x,t)\,dx. \tag{T2.91}$$

Following the procedure in (T2.78), we now proceed to calculate the expectation value of the observable p_x in the state Ψ:

$$\begin{aligned}\langle\, p_x\,\rangle_\Psi &= \int_{-\infty}^{\infty} dx\,\Psi^*(x,t)\,\widehat{p}_x\,\Psi(x,t) = \int_{-\infty}^{\infty} dx\,(\widehat{p}_x\Psi(x,t))^*\,\Psi(x,t)\\ &= \int_{-\infty}^{\infty} dx \left(\widehat{p}_x \int_{-\infty}^{\infty} dp\,\Phi(p,t)\,\psi_p(x)\right)^* \Psi(x,t).\end{aligned}$$

Here we replace $\widehat{p}_x\psi_p(x)$ with $p\psi_p(x)$ and change the order of the integrations:

$$\begin{aligned}\langle\, p_x\,\rangle_\Psi &= \int_{-\infty}^{\infty} dp\,\Phi^*(p,t)\,p\left(\int_{-\infty}^{\infty} dx\,\psi_p^*(x)\,\Psi(x,t)\right)\\ &= \int_{-\infty}^{\infty} \Phi^*(p,t)\,p\,\Phi(p,t)\,dp = \int_{-\infty}^{\infty} p\,|\Phi(p,t)|^2 dp.\end{aligned}$$

On the other hand we know that

$$\langle\, p_x\,\rangle_\Psi = \int_{-\infty}^{\infty} p\,P(p)\,dp,$$

where $P(p)$ is the probability density in "p space" [so that $P(p)dp$ is the probability of measuring the momentum p_x in the interval $(p, p+dp)$]. Thus, the physical interpretation of the "expansion coefficient" (the Fourier transform $\Phi(p,t)$) is:

When the system is in the state $\Psi(x,t)$ before the measurement, the probability of measuring p_x in the interval $(p, p+dp)$ is

$$P(p)dp = |\Phi(p,t)|^2 dp = |\langle\, \psi_p, \Psi\,\rangle|^2\,dp \equiv \left|\int \psi_p^*(x)\Psi(x,t)\,d\tau\right|^2 dp. \tag{T2.92}$$

Thus the probability density in "p space" is the square of the Fourier transform $\Phi(p,t)$. This is analoguous to $|\Psi(x,t)|^2$ being the probability density in x space .

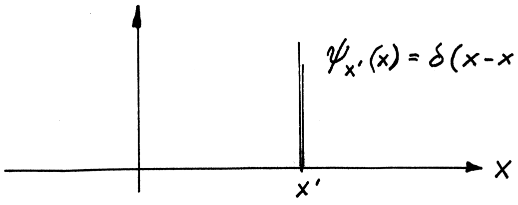
2.5.g The position eigenfunctions $\delta(x-x')\equiv\psi_{x'}(x)$ as a basis (the "x-basis")

The relation

$$x\delta(x-x')=x'\delta(x-x') \qquad \text{(T2.93)}$$

can be interpreted as an eigenvalue equation for the operator $\widehat{x}=x$ (multiplication by x). Here, x' is the eigenvalue, and we see that the x-dependent eigenfunction corresponding to this eigenvalue is

$$\delta(x-x')\equiv\psi_{x'}(x) \qquad \text{(a function of } x\text{).}$$



(For comparison, $\psi_p(x)$ is an eigenfunction of the momentum operator $\widehat{p}_x$ with the eigenvalue p.) The continuous spectrum $x'\in(-\infty,\infty)$ of eigenvalues implies that we must use delta-function normalization:

$$\int_{-\infty}^{\infty}\psi^*_{x'}(x)\psi_{x''}(x)dx=\int_{-\infty}^{\infty}\delta(x-x')\delta(x-x'')dx=\delta(x'-x''), \qquad \text{(T2.94)}$$

in analogy with the normalization

$$\int_{-\infty}^{\infty}\psi^*_p(x)\psi_{p'}(x)dx=\delta(p-p')$$

for the momentum eigenfunctions.

The position eigenfunctions $\psi_{x'}(x)=\delta(x-x')$ may very well be used as a basis for the "vector space of square-integrable functions" (the Hilbert space), even if this basis itself does not belong to this space. (We remember that the same was the case with the momentum eigenfunctions.) As an example, we may expand the wave function Ψ of a physical system in the position basis. This expansion in fact follows directly from the identity

$$\Psi(x,t)=\int_{-\infty}^{\infty}\Psi(x',t)\delta(x-x')dx'=\int_{-\infty}^{\infty}\Psi(x',t)\psi_{x'}(x)dx'. \qquad \text{(T2.95)}$$

Thus the "expansion coefficient" is $\Psi(x',t)$. This expansion is analogous to the Fourier expansion

$$\Psi(x,t)=\int_{-\infty}^{\infty}\Phi(p,t)\psi_p(x)dp.$$

Inspired by (T2.92), we can then interpret $|\Psi(x',t)|^2dx'$ as the probability of measuring the position in the interval $(x',x'+dx')$. We recognize this as the probability interpretation of the wave function. This illustrates that the role played by $|\Psi(x,t)|^2$ in position space is the same as the role played by $|\Phi(p,t)|^2$ in momentum space.

2.6 The momentum-space formulation of quantum mechanics***[9]

This "similarity" between the position-space and momentum-space probability densities is not accidental. As explained in section 4.6 in Hemmer and in 3.9 in B&J, it is straightforward to obtain a formulation of the theory in which the Fourier transform $\Phi(p,t)$ of $\Psi(x,t)$ plays the role of a "wave function" in momentum space. This role is analogous to that played by the ordinary wave function $\Psi(x,t)$ in the **position-space formulation of quantum mechanics**, which we are now beginning to get used to, and which is most commonly used on the introductory level.

In the new **momentum-space formulation of quantum mechanics**, we already know how to obtain the expectation values of observables which depend only on p_x, like e.g. $K = p_x^2/2m$. Since the probability density in momentum space is $|\Phi(p,t)|^2$, we have that

$$\langle\, F(p_x)\,\rangle_\Phi = \int_{-\infty}^{\infty} |\Phi(p,t)|^2 F(p)dp = \int_{-\infty}^{\infty} \Phi^*(p,t)\, F(p)\, \Phi(p,t)\, dp, \qquad \text{(T2.96)}$$

which is analogous to

$$\langle\, V(x)\,\rangle_\Psi = \int_{-\infty}^{\infty} \Psi^*(x,t)\, V(x)\, \Psi(x,t)\, dx$$

in the position-space formulation. The "moral" is that in the momentum-space formulation, the observable p_x is represented by an operator which simply is (multiplication by) the *number* p,

$$\widehat{p}_x = p. \qquad \text{(T2.97)}$$

This is analogous to $\widehat{x} = x$ in the position-space formulation.

What about the operators representing x and functions of x (like e.g. $V(x)$) in the new formulation? To find the answer, we shall assume that the potential $V(x)$ can be expanded in a Taylor series,

$$V(x) = \sum_n v_n x^n,$$

where the expansion coefficients are v_n. The expectation values of x and powers of x can now be found starting with the old formulation, where the expectation value of x^n is

$$\begin{aligned} \langle\, x^n\,\rangle &= \int_{-\infty}^{\infty} \Psi^*(x,t)\, x^n\, \Psi(x,t)\, dx = \int_{-\infty}^{\infty} (x^n\Psi)^*\Psi\, dx \\ &= \int_{-\infty}^{\infty} dx \left(x^n \int_{-\infty}^{\infty} dp\, \Phi(p,t)\, \psi_p(x) \right)^* \Psi(x,t). \end{aligned}$$

Here we apply the identity

$$x\, e^{ipx/\hbar} = \left(\frac{\hbar}{i}\frac{\partial}{\partial p} \right) e^{ipx/\hbar}, \qquad \text{(T2.98)}$$

which means that

$$x^n\, \psi_p(x) = \left(\frac{\hbar}{i}\frac{\partial}{\partial p} \right)^n \psi_p(x). \qquad \text{(T2.99)}$$

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[9] Sections marked with *** are not compulsory in FY1006/TFY4215.

Inserting this and rearranging we then have

$$\begin{aligned}
\langle\, x^n \,\rangle &= \int_{-\infty}^{\infty} dx \left(\int_{-\infty}^{\infty} dp\, \Phi(p,t) \left(\frac{\hbar}{i}\frac{\partial}{\partial p} \right)^n \psi_p(x) \right)^* \Psi(x,t) \\
&= \int_{-\infty}^{\infty} dp\, \Phi^*(p,t) \left(-\frac{\hbar}{i}\frac{\partial}{\partial p} \right)^n \underbrace{\int_{-\infty}^{\infty} dx\, \psi_p^*(x)\Psi(x,t)}_{\Phi(p,t)} \\
&= \int_{-\infty}^{\infty} dp\, \Phi^*(p,t) \left(-\frac{\hbar}{i}\frac{\partial}{\partial p} \right)^n \Phi(p,t). \qquad \text{(T2.100)}
\end{aligned}$$

Comparing this expression with the general "sandwich" recipe for expectation values,

$$\langle\, F \,\rangle_\Phi = \int_{-\infty}^{\infty} dp\, \Phi^*(p,t)\, \widehat{F}\, \Phi(p,t), \qquad \text{(T2.101)}$$

we can conclude that the observable x^n is represented in the momentum-space formulation by the n^{th} power of the operator

$$\widehat{x} = -\frac{\hbar}{i}\frac{\partial}{\partial p}. \qquad \text{(T2.102)}$$

For a *function* of x like e.g. $V(x) = \sum v_n x^n$ we find that

$$\langle\, V(x) \,\rangle_\Phi = \int_{-\infty}^{\infty} dp\, \Phi^*(p,t) \left[\sum_n v_n \left(-\frac{\hbar}{i}\frac{\partial}{\partial p} \right)^n \right] \Phi(p,t). \qquad \text{(T2.103)}$$

Thus the potential energy is in the new formulation represented by the operator

$$\sum_n v_n \left(-\frac{\hbar}{i}\frac{\partial}{\partial p} \right)^n \equiv \widehat{V}\left(-\frac{\hbar}{i}\frac{\partial}{\partial p} \right).$$

This is called an **operator function**, and the Taylor expansion on the left shows exactly what we mean by this. As an example, the harmonic-oscillator potential $V(x) = \frac{1}{2}m\omega^2x^2$ is in this formulation represented by the operator $\widehat{V} = \frac{1}{2}m\omega^2(-\frac{\hbar}{i}\frac{\partial}{\partial p})^2$.

We have now learnt how to calculate expectation values of observables depending on x and p_x in the new formulation, from the "wave function" $\Phi(p,t)$. But can we be sure that this function contains all possible information about the system, as is the case for $\Psi(x,t)$ according to the wave-function postulate on page 8? The answer is yes: If we know the function $\Phi(p,t)$, then we also know $\Psi(x,t)$, via the Fourier integral

$$\Psi(x,t) = \int_{-\infty}^{\infty} \Phi(p,t)\, \psi_p(x)\, dp,$$

and vice versa, via the Fourier transform

$$\Phi(p,t) = \int_{-\infty}^{\infty} \psi_p^*(x)\, \Psi(x,t)\, dx.$$

Thus the two functions contain the same information.

But isn't $\Psi(x,t)$ still more special, since it satisfies a wave equation, the Schrödinger equation? The answer is no: There exists a wave equation also for $\Phi(p,t)$. We can find this equation by taking the derivative $i\hbar(\partial/\partial t)\Phi(p,t)$ as our starting point: Using the last formula above, we find that

$$\begin{aligned}
\underline{i\hbar\frac{\partial}{\partial t}\Phi(p,t)} &= \int_{-\infty}^{\infty}\psi_p^*(x)\, i\hbar\frac{\partial}{\partial t}\Psi(x,t)\,dx \qquad \left(i\hbar\frac{\partial}{\partial t}\Psi = \left[\widehat{p}_x^2/2m+V(x)\right]\Psi\right)\\
&= \int_{-\infty}^{\infty}\psi_p^*(x)\underbrace{\left[\widehat{p}_x^2/2m+V(x)\right]}_{\text{hermitesk}}\Psi(x,t)\,dx\\
&= \int_{-\infty}^{\infty}\left(\left[\widehat{p}_x^2/2m+\sum_n v_n x^n\right]\psi_p(x)\right)^*\Psi(x,t)\,dx\\
&= \int_{-\infty}^{\infty}\left(\left[p^2/2m+\sum_n v_n\left(\frac{\hbar}{i}\frac{\partial}{\partial p}\right)^n\right]\psi_p(x)\right)^*\Psi(x,t)\,dx.
\end{aligned}$$

Here we have applied the identities

$$\widehat{p}_x\psi_p(x) = p\psi_p(x) \qquad \text{and} \qquad x\,\psi_p(x) = \left(\frac{\hbar}{i}\frac{\partial}{\partial p}\right)\psi_p(x).$$

In the last expression we can move the operator $[\;\;]^*$ to the left of the integral, because it does not depend on x. We then have

$$\begin{aligned}
\cdots &= \left[p^2/2m+\sum_n v_n\left(-\frac{\hbar}{i}\frac{\partial}{\partial p}\right)^n\right]\underbrace{\int_{-\infty}^{\infty}\psi_p^*(x)\Psi(x,t)\,dx}_{\Phi(p,t)}\\
&= \underline{\left[p^2/2m+\widehat{V}\left(-\frac{\hbar}{i}\frac{\partial}{\partial p}\right)\right]\Phi(p,t)} \equiv \underline{\widehat{H}\Phi(p,t)}. \qquad \text{(T2.104)}
\end{aligned}$$

This must be called a success: $\Phi(p,t)$ does satisfy a wave equation, and the form of this equation allows us to call it a Schrödinger equation.

Thus we have two equivalent versions of quantum mechanics, the **position-space formulation** and the **momentum-space formulation**. With the symbols x,y,z (or $x_i,\ i = 1,..,3$) for the cartesian coordinates, the situation can be summarized by the following table, where we see that both wave functions satisfy the Schrödinger equation, with a Hamiltonian given by the general formula

$$\widehat{H}(\widehat{x}_i,\widehat{p}_i) = \frac{\widehat{p}_x^2+\widehat{p}_y^2+\widehat{p}_z^2}{2m}+\widehat{V}(\widehat{x},\widehat{y},\widehat{z}).$$

Example: Free particle

For a free particle ($V = 0$) we see that the Schrödinger equation in the momentum-space formulation looks like this:

$$i\hbar\frac{\partial\Phi(p,t)}{\partial t} = \frac{p^2}{2m}\Phi(p,t) \qquad (p = p_x)\,.$$

Here, $\partial/\partial t$ means differentiation with p kept fixed. Then it is easy to see that the time-dependent wave function in momentum space becomes

$$\Phi(p,t) = \Phi(p,0)\,e^{-i(p^2/2m)t/\hbar}. \qquad \text{(T2.105)}$$

	Position-space formulation	Momentum-space formulation
Wave function	$\Psi(x,y,z,t)$	$\Phi(p_x,p_y,p_z,t)$
Operator $\widehat{x}_i$	x_i	$-\dfrac{\hbar}{i}\dfrac{\partial}{\partial p_i}$
Operator $\widehat{p}_i$	$\dfrac{\hbar}{i}\dfrac{\partial}{\partial x_i}$	p_i
Wave equation	$i\hbar\,\dfrac{\partial\Psi}{\partial t}=\widehat{H}(\widehat{x}_i,\widehat{p}_i)\Psi$	$i\hbar\,\dfrac{\partial\Phi}{\partial t}=\widehat{H}(\widehat{x}_i,\widehat{p}_i)\Phi$

Here, $\phi(p,0)$ is the momentum-space wave function at $t=0$, which we are allowed to prepare arbitrarily, but we assume that it is normalized:

$$\int_{-\infty}^{\infty}|\Phi(p,0)|^2dp=1.$$

From the solution (T2.105) we see that the probability density in momentum space becomes *time independent* for the free particle,

$$|\Phi(p,t)|^2=|\phi(p,0)|^2,$$

and this should not be surprising. The same should then be the case for all purely p-dependent observables, like e.g.

$$\langle\, p\,\rangle=\int_{-\infty}^{\infty}\Phi^*(p,t)\,p\,\Phi(p,t)\,dp=\int_{-\infty}^{\infty}\Phi^*(p,0)\,p\,\Phi(p,0)\,dp=\langle\, p\,\rangle_{t=0}\,,$$

$\langle\, p^2\,\rangle$, Δp, etc. We can also find out how the expectation value of the position behaves: From (T2.53) and (T2.55) we have

$$\begin{aligned}
\langle\, x\,\rangle_t &= \int_{-\infty}^{\infty}\Phi^*(p,t)\left(-\frac{\hbar}{i}\frac{\partial}{\partial p}\right)\Phi(p,t)\,dp\\
&= \int_{-\infty}^{\infty}\Phi^*(p,0)e^{i(p^2/2m)t/\hbar}\left[-\frac{\hbar}{i}\frac{\partial}{\partial p}\,\Phi(p,0)-\Phi(p,0)\,\frac{\hbar}{i}\frac{\partial}{\partial p}\left(-\frac{ip^2t}{2m\hbar}\right)\right]e^{i(p^2/2m)t/\hbar}\,dp\\
&= \int_{-\infty}^{\infty}\Phi^*(p,0)\left(-\frac{\hbar}{i}\frac{\partial}{\partial p}\right)\Phi(p,0)\,dp+\frac{t}{m}\int_{-\infty}^{\infty}\Phi^*(p,0)\,p\,\Phi(p,0)\,dp\\
&= \langle\, x\,\rangle_{t=0}+\frac{\langle\, p\,\rangle}{m}\,t.
\end{aligned}$$

Thus the expectation value $\langle\, x\,\rangle_t$ is moving with constant velocity $\langle\, p\,\rangle/m$, from $\langle\, x\,\rangle_{t=0}$ at $t=0$. This agrees with Newton's first law.

2.7 Stationary and non-stationary states

2.7.a Stationary states **(Hemmer p 26, Griffiths p 21, 3.5 in B&J)**

The concept of a stationary state was first introduced in Tillegg 1, to denote the *the physical state* of e.g. the "ground state" of the hydrogen atom, following Bohr's idea. On the theoretical side we saw that when Schrödinger was able to find an eigenfunction of the Hamiltonian $\widehat{H}$,

$$\widehat{H}\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}),$$

then the function

$$\Psi_n(\mathbf{r},t) = \psi_n(\mathbf{r})e^{-iE_nt/\hbar}$$

is a solution of the (time-dependent) Schrödinger equation. [10]

We call this a *stationary solution* (of the Schrödinger equation), because it gives a theoretical description of the physical state. In the literature, it is common to use the notion of a "stationary state" to denote both the physical state and the and the corresponding theoretical solution $\Psi(\mathbf{r},t)$ of the Schrödinger equation.

The stationary states emerge in a natural way when we try to separate the time- and space-dependence by looking for solutions of the Schrödinger equation on the form

$$\Psi(x,t) = \psi(x)f(t).$$

As you can see e.g. on page 26 in Hemmer, this separation is possible only if

- (i) $\widehat{H}$ is time-$\underline{\text{independent}}$, and
- (ii) $\psi(x)$ is an eigenfunction of $\widehat{H}$.

Thus, ψ must be a solution of the time-independent Schrödinger equation, $\widehat{H}\psi_E(x)= E\psi_E(x)$.

It is then straightforward to find $f(t)$. The time-*dependent* Schrödinger equation gives

$$i\hbar\,\frac{\partial f}{\partial t}\cdot\psi_E(x) = f(t)\,\widehat{H}\psi_E(x) = f(t)\,E\,\psi_E(x).$$

Here, the partial derivative $\partial/\partial t$ implies differentiation with respect to t with x kept fixed. And with fixed x it is easy to integrate the above equation over time, from 0 to t:

$$\frac{df}{f} = -\frac{iE}{\hbar}\,dt \qquad \Longrightarrow \qquad \ln f(t) = \ln f(0) - \frac{iEt}{\hbar}, \qquad \Longrightarrow$$

$$f(t) = f(0)\,e^{-iEt/\hbar}.$$

The constant $f(0)$ can be absorbed into $\psi(x)$, so that the solution becomes

$$\boxed{\Psi_E(x,t) = \psi_E(x)\,e^{-iEt/\hbar}.} \qquad \text{(T2.106)}$$

As already mentioned, this is called a **stationary solution** of the Schrödinger equation, because

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[10] See also the discussion of a particle in a box, in section 2.1.

- the probability density $|\Psi_E(x,t)|^2 = |\psi_E(x)|^2$ is time independent (does not "move")
- all observables which do not depend explicitly on the time, like e.g. x, p_x, E etc, have time-independent expectation values in such a stationary state $\Psi_E(x,t)$.This is because for such an observable $F = F(x,p_x)$ we have:

$$\begin{aligned} \langle\, F \,\rangle_{\Psi_E} &= \int \Psi_E^*(x,t)\, \widehat{F}(x,\widehat{p}_x)\, \Psi_E(x,t)dx \\ &= \int \psi_E^*(x)\, \widehat{F}(x,\widehat{p}_x)\, \psi_E(x)dx = \text{constant}, \end{aligned} \qquad \text{(T2.107)}$$

(since the time-dependent exponentials in the integrand cancel). This means that the exponential function $\exp(-iEt/\hbar)$ in reality is without physical meaning for a stationary state; it has no measurable consequences. Thus, in a stationary state there is no measurable *time development*; there is no *process* taking place; *nothing "happens"*. So the state really deserves to be called stationary.

Why then are we so interested in the energy eigenfunctions and the corresponding stationary states? There are (at least) four reasons:

Reason 1: When a system has its lowest possible energy (is in its ground state), all the properties of the system in this state are determined by the ground-state energy eigenfunction $\psi(\mathbf{r})$. Even if nothing "happens" in this state, the wave function contains a lot of interesting information: It determines all the physical properties of the system in its ground state, such as the *form*, the *size* and the *energy.* This holds both for isolated atoms and for more complicated systems, like more or less complex molecules, crystals, etc. The same holds for excited states (where both the size and the form may differ very much from those of the ground state).

Reason 2: Since $\psi_E(x)$ [and also $\Psi_E(x,t) = \psi_E(x)\exp(-iEt/\hbar)$] are eigenfunctions of $\widehat{H}$ (and $\widehat{H}^2$) with eigenvalues E (and E^2), we can state that the *energy is sharply defined* in a stationary state, meaning that the uncertainty in the energy is $\Delta E = 0$. [Remember that $(\Delta E)^2 = \langle\, (E - \langle\, E\,\rangle)^2\,\rangle = \langle\, E^2\,\rangle - \langle\, E\,\rangle^2$; cf section 2.4.b above.] These energies are important in **processes** where the system is **excited** or **de-excited**. (Cf spectral lines.)

2.7.b Non-stationary states

Reason 3: According to the superposition principle, also an arbitrary linear combination of the stationary solutions $\Psi_n(x,t) = \psi_n(x)\exp(-iE_nt/\hbar)$ is a solution of the Schrödinger equation, and therefore describes a possible physical state of the system (cf the discussion of the particle in a box in section 2.1):

$$\boxed{\Psi(x,t) = \sum_n c_n\, \Psi_n(x,t) = \sum_n c_n\, \psi_n(x)\, e^{-iE_nt/\hbar}.} \qquad \text{(T2.108)}$$

Here the coefficients c_n are arbitrary complex constants (independent of x and t). It can be shown that $\Psi(x,t)$ is normalized if $\sum_n |c_n|^2 = 1$ (provided that the set $\psi_n(x)$ is orthonormalized). It can also be shown that the expression above is the most general solution of the Schrödinger equation. This means that *all* solutions of the Schrödinger equation can be expanded in terms of the stationary solutions.

If the sum above above contains terms with *different* energies E_n, the sum is *not* an eigenfunction of the Hamiltonian $\widehat{H}$. Then $\Psi(x,t)$ is a non-stationary solution of the Schrödinger equation and describes a non-stationary physical state for the system. For such a state it is easy to see that the probability density $|\Psi(x,t)|^2$ and (some of) the expectation values $\langle\, F\,\rangle_\Psi$ will depend on time (contrary to the case of stationary states). The reason is of course that the phase factors $\exp(-iE_nt/\hbar)$ are "running around the complex unit circle with different speeds", or different periods $T_n = 2\pi\hbar/E_n$, if you like. Here we observe that these phase factors (or rather the *ratios* between them) are in fact important. Such non-stationary states are always needed if we want to describe a **process**, where something *happens*.

Reason 4: A generic problem in quantum mechanics is to find the wave function $\Psi(x,t)$ at an arbitrary time t when the system is prepared in a given state $\Psi(x,t_0)$ at some initial time t_0, e.g. $t_0 = 0$. When the potential is time-independent, we can solve this problem by expanding the unknown solution $\Psi(x,t)$ in terms of the stationary states, which form a complete set:

$$\Psi(x,t) = \sum_n c_n\psi_n(x)\,e^{-iE_nt/\hbar}.$$

Thus the problem is essentially solved if we can determine the expansion coefficients c_n. These are determined by the initial state. By setting $t = 0$ in the above expansion, we have

$$\Psi(x,0) = \sum_n c_n\,\psi_n(x). \tag{T2.109}$$

With our experience from section 2.5.b, we now see that c_n is the projection of $\Psi(x,0)$ onto the eigenfunction $\psi_n(x)$, but it does not hurt to repeat the calculation: By projecting $\Psi(x,0)$ onto the eigenstate $\psi_n(x)$ we find that

$$\underline{\langle\,\psi_n,\Psi(0)\,\rangle} = \left\langle\,\psi_n,\sum_k c_k\psi_k\,\right\rangle = \sum_k c_k\,\langle\,\psi_n,\psi_k\,\rangle = \sum_k c_k\delta_{nk} = \underline{c_n}, \quad \text{q.e.d.} \tag{T2.110}$$

Thus the time-dependent wave function is

$$\Psi(x,t) = \sum_n \langle\,\psi_n,\Psi(0)\,\rangle\;\psi_n(x)\,e^{-iE_nt/\hbar}, \tag{T2.111}$$

where

$$\langle\,\psi_n,\Psi(0)\,\rangle \equiv \int_{-\infty}^{\infty}\psi_n^*(x)\Psi(x,0)dx. \tag{T2.112}$$

The *trivial* example is when the initial state is one of the energy eigenstates, that is when $\Psi(x,0) = \psi_i(x)$. (i for "initial".) Then the recipe above gives

$$c_n = \langle\,\psi_n,\Psi(0)\,\rangle = \langle\,\psi_n,\psi_i\,\rangle = \delta_{ni},$$

and the system *continues* to be in the corresponding stationary state:

$$\Psi(x,t) = \sum_n \delta_{ni}\psi_n(x)\,e^{-iE_nt/\hbar} = \psi_i(x)\,e^{-iE_it/\hbar} \equiv \Psi_i(x,t).$$

Conclusion: Given a problem for which the Hamiltonian is time independent, the general strategy simply is to find the complete set $\psi_n(x)$ of energy eigenfunctios, and the corresponding stationary solutions $\Psi_n(x,t) = \psi_n(x)\exp(-iE_nt/\hbar)$ of the Schrödinger equation.

2.8 Conservation of probability

This section is beautifully described in section 2.6.1 in Hemmer. See also 3.2 in B&J. Some comments:

The normalization is conserved

For a *stationary* state the normalization condition is

$$\Psi_E(\mathbf{r},t) = \psi_E(\mathbf{r})e^{-iEt/\hbar} \qquad \text{and} \qquad \int |\Psi_E(\mathbf{r},t)|^2 d^3r = \int |\psi_E(\mathbf{r})|^2 d^3r = 1.$$

Here we see that if the wave function is normalized at $t = 0$, then it is normalized for all times; the probability is *conserved.* The probability must of course also be conserved for non-stationary states $\Psi(\mathbf{r},t)$ — in our non-relativistic theory the particle must always be *somewhere*, and then the integral over the probability density $|\Psi(\mathbf{r},t)|^2$ must be equal to 1 at any time.[11] That this actually is the case can be seen from the expansion in terms of stationary (and orthonormalized) states,

$$\Psi(\mathbf{r},t) = \sum_n c_n \Psi_n(\mathbf{r},t),$$

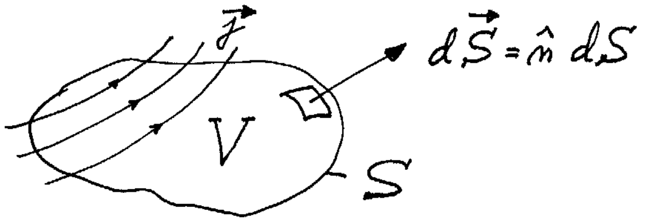
where the coefficients c_n are time independent. As discussed in section 2.1 above, the cross terms in the product of the two sums $\Psi^*(\mathbf{r},t)$ and $\Psi(\mathbf{r},t)$ in the normalization integral will vanish under the integration; cf the normalization condition which is

$$\int \Psi^*\Psi d^3r = \int \left(\sum_m c_m^*\Psi_m^*\right)\left(\sum_n c_n\Psi_n\right) d^3r = \sum_{nm} c_m^* c_n \underbrace{\int \Psi_m^*\Psi_n d^3r}_{\delta_{mn}} = \sum_n |c_n|^2 = 1. \tag{T2.113}$$

Clearly, if this condition is satisfied for $t = 0$, it will be satisfied for all times. Thus the normalization is "conserved".

Probability conservation on integral form

If the probability $\int_V \rho(\mathbf{r},t)d^3r$ of finding the particle inside some volume V is increasing, the total probability current entering this volume must be positive.



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[11] In relativistic theory — and in reality — it is not that simple; particles can be created or annihilated.

Therefore there must exist a **probability current density** $\mathbf{j}(\mathbf{r},t)$, in such a way that the current *entering* the volume is given by a surface integral $-\int_S \mathbf{j}{\cdot}d\mathbf{S}$. (Note that $d\mathbf{S} = \hat{\mathbf{n}}dS$ points *outwards.*) In order to have a conserved probability we must then have

$$\frac{d}{dt}\int_V \rho(\mathbf{r},t)d^3r = \int_V \frac{\partial\rho}{\partial t}\,d^3r = -\int_S \mathbf{j}{\cdot}d\mathbf{S} \overset{\text{G.t}}{=} -\int_V \boldsymbol{\nabla}{\cdot}\mathbf{j}\,d^3r. \qquad \text{(T2.114)}$$

Here we have used Gauss' theorem (the divergence theorem) to transform the surface integral into a volume integral over the divergence of the probability current density. This equation expresses probability conservation on integral form.

Differential form, the continuity equation

Since the above conservation law on integral form is valid for an arbitrary volume V (with arbitrary position and size), we see that ρ and $\mathbf{j}$ must satisfy the **continuity equation**:

$$\boxed{\frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}{\cdot}\mathbf{j} = 0.} \qquad \begin{pmatrix}\text{continuity}\\ \text{equation}\end{pmatrix} \qquad \text{(T2.115)}$$

This conservation law on differential form is valid not only for probability, but also for electric charge in electrodynamics, mass in hydrodynamics, etc.

The expression for j

As shown in Hemmer or in B&J, it is fairly straightforward to find an expression for the probability current density $\mathbf{j}$. Here we show this for the one-dimensional case. Using the Schrödinger equation,

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

we have

$$\begin{aligned}\frac{\partial\rho}{\partial t} &= \frac{\partial}{\partial t}(\Psi^*\Psi) = \Psi^*\,\frac{\partial\Psi}{\partial t} + \Psi\,\frac{\partial\Psi^*}{\partial t}\\ &= -\frac{\hbar}{2mi}\left(\Psi^*\,\frac{\partial^2\Psi}{\partial x^2} - \Psi\,\frac{\partial^2\Psi^*}{\partial x^2}\right) = -\frac{\hbar}{2mi}\,\frac{\partial}{\partial x}\left(\Psi^*\,\frac{\partial\Psi^*}{\partial x} - \Psi\,\frac{\partial\Psi^*}{\partial x}\right).\end{aligned}$$

(In the next to the last step, the terms with $V(x,t)$ cancel. The last step is most easily taken backwards.) Since $z + z^* = 2\Re\text{e}(z)$, this can be re-written as

$$\frac{\partial\rho}{\partial t} = -\frac{\partial}{\partial x}\left(\Psi^*\,\frac{\hbar}{2mi}\frac{\partial}{\partial x}\Psi + \Psi\,\frac{\hbar}{2m(-i)}\frac{\partial}{\partial x}\Psi^*\right) = -\frac{\partial}{\partial x}\Re\text{e}\left(\Psi^*\,\frac{\hbar}{mi}\frac{\partial}{\partial x}\,\Psi\right).$$

In one dimension, everything depends only on x and t, and the probability current density must be directed in the x direction. From the above formula we therefore have

$$\frac{\partial\rho}{\partial t} + \frac{\partial j_x}{\partial x} = 0, \qquad j_x = \Re\text{e}\left(\Psi^*\,\frac{\widehat{p}_x}{m}\,\Psi\right). \qquad \text{(T2.116)}$$

In three dimensions, this can be generalized to

$$\boxed{\frac{\partial\rho}{\partial t}+\boldsymbol{\nabla}\cdot\mathbf{j}=0,} \qquad \boxed{\mathbf{j}=\Re\mathrm{e}\left(\Psi^*\,\frac{\widehat{\mathbf{p}}_x}{m}\,\Psi\right).} \tag{T2.117}$$

For a normalized (localized) state, the wave function, and hence also **j**, must approach zero "far away" from where the particle is localized. Therefore, if we let the volume in (T2.114) become sufficiently large, the surface integral $\int_S \mathbf{j}\cdot d\mathbf{S}$ must clearly approach zero:

$$\frac{d}{dt}\int_V \rho(\mathbf{r},t)d^3r=-\int_V \boldsymbol{\nabla}\cdot\mathbf{j}\,d^3r=0.$$

In this limit, the total probability inside the volume V therefore is constant in time; proving once again that the normalization is "conserved", as we found above.

Probability current density for de Broglie wave

The formula for the current density can also be used for non-localized states as e.g. the de Broglie wave (and the momentum eigenfunction)

$$\Psi_{\mathbf{p}}(\mathbf{r},t)=\psi_{\mathbf{p}}(\mathbf{r})e^{-iEt/\hbar},\qquad \psi_{\mathbf{p}}(\mathbf{r})=(2\pi\hbar)^{-3/2}e^{i\mathbf{p}\cdot\mathbf{r}/\hbar},\qquad E=p^2/2m. \tag{T2.118}$$

We note that **j** is time independent for this state (and for all other stationary states):

$$\mathbf{j}=\Re\mathrm{e}\left[\Psi^*_{\mathbf{p}}\frac{\hbar}{im}\boldsymbol{\nabla}\Psi_{\mathbf{p}}\right]=\Re\mathrm{e}\left[\psi^*_{\mathbf{p}}\frac{\hbar}{im}\boldsymbol{\nabla}\psi_{\mathbf{p}}\right]. \tag{T2.119}$$

It should also be noticed that ψ must be complex to give a non-zero current density. In this particular example, we have that $\boldsymbol{\nabla}e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}=i(\mathbf{p}/\hbar)e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}$, so that the current density becomes

$$\mathbf{j}=|\psi_{\mathbf{p}}|^2\frac{\mathbf{p}}{m}. \tag{T2.120}$$

(Repeat this calculation.) Thus we arrive at the sensible result that $\mathbf{j}=\rho\,\mathbf{v}$, where $\mathbf{v}=\mathbf{p}/m$ is the classical velocity.

A small exercise: It can be shown that for a free particle with mass m, the initial state

$$\Psi(x,0)=(2\pi\sigma^2)^{-1/4}e^{-x^2/4\sigma^2}e^{ip_0x/\hbar}$$

will give a wave packet moving with the group velocity $v_x=p_0/m$. The *width* of this wave packet increases when t increases from zero. This increase of the width is called dispersion, and is independent of the value chosen for p_0.

a. Show that if we choose $p_0=0$, then the current density is equal to zero for $t=0$, $j(x,0)=0$.

b. Why must (still assuming that $p_0=0$) $j(x,t)$ be different from zero for for $t>0$?

c. Show that with $p_0 \neq 0$, the current density for $t = 0$ is

$$j(x,0) = |\Psi(x,0)|^2 \frac{p_0}{m} = \rho(x,0) v_x.$$