# Quantum Mechanics — Lecture notes for PHYS223

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These lecture notes lay out the mathematical and interpretational framework of quantum mechanics and describe how this theory can be utilised to describe common physical systems and phenomena. Starting from the Schrödinger equation, we study a number of exactly solvable problems, including one-dimensional potentials, angular momentum quantization, spin, and the hydrogen atom, and also provide systematic approximations for not exactly solvable problems. The physical content of the mathematical solutions is discussed in terms of probabilities and expectation values. The latter parts of the notes concern temporal dynamics and systems composed of more than one particle.

## CONTENTS

# I. WAVES ARE PARTICLES, PARTICLES ARE WAVES

We start by revisiting two experiments which contravene the laws of classical physics. The observations match with phenomenological explanations that relate particles and waves. Quantum mechanics extends this phenomenology into a consistent general framework.

## A. Compton scattering: waves are particles

Compton scattering occurs when X-rays [an electromagnetic (EM) wave of a very small wave length $\lambda$] hit an electron at rest (e.g., an electron bound in a solid). In the scattering event the wave is deflected and the electron is accelerated to a large velocity $\mathbf{v}$, i.e., it acquires a large final momentum $\mathbf{p}_e$. (We use boldface letters to denote vectors in three-dimensional space.) One observes that the wave changes its wave length to $\lambda' > \lambda$, and that this change depends on the deflection angle $\phi$ (i.e., the position of the detector which collects the scattered wave).

Classical electromagnetism does not permit such a change of wave length. In this theory, a

plane wave with fixed propagation direction **n** has space and time dependence

$$\exp(i\mathbf{k} \cdot \mathbf{r} - i\omega t), \tag{1.1}$$

where $\omega = 2\pi f$ is the angular frequency (with $f$ the usual frequency), while $\mathbf{k} = k\mathbf{n}$ is the wave vector, which points into the propagation direction and has length $|\mathbf{k}| = k = 2\pi/\lambda$. The scalar $k$ is called the wave number, and is strictly related to the angular frequency via the relation $\omega/k = c$, where $c$ is the speed of light. Upon scattering off a static object, the frequency of the wave does not change, and so its wave length cannot change as well.

However, a phenomenological explanation of the observations can be given when one assumes that the X-rays are composed of particles, called photons, which carry specific amounts (quanta) of *energy*

$$E = \hbar\omega \tag{1.2}$$

and *momentum*

$$\mathbf{p} = \hbar\mathbf{k}, \tag{1.3}$$

where

$$\hbar = 1.054\,571\,726\,(47) \times 10^{-34}\mathrm{Js} \tag{1.4}$$

is the *reduced Planck's constant* (Planck's constant itself is defined as $h = 2\pi\hbar$). Equation (1.2) is known as the *Planck relation*, while Eq. (1.3) is known as the *de Broglie relation*.

These photons move at a velocity given by the speed of light $c = \lambda f = \omega/k$. According to the kinematic relations of special relativity, they hence carry no mass and obey $E = cp$. The electron has a finite mass $m$ and rest energy $E_e = mc^2$ before the collision, which changes to $E'_e = \sqrt{m^2c^4 + p_e^2c^2}$ after the collision. From the conservation laws for energy $\hbar\omega + E_e = \hbar\omega' + E'_e$ and momentum $\hbar\mathbf{k} = \hbar\mathbf{k}' + \mathbf{p}_e$ it follows[1] that

$$\lambda' - \lambda = \frac{2\pi\hbar}{mc}(1 - \cos\phi). \tag{1.5}$$

This indeed recovers the experimentally observed change of the wave length.

### Points to remember

- De-Broglie relation $\mathbf{p} = \hbar\mathbf{k}$

- Planck relation $E = \hbar\omega$

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[1] using $\omega = kc$, $k = 2\pi/\lambda$, and $\hbar kc + E_e = \hbar k'c + E'_e \Rightarrow$
$[\hbar(k - k') + mc]^2 = m^2c^2 + \underbrace{\hbar^2(k^2 + k'^2 - 2kk'\cos\phi)}_{p_e^2, \text{ since } \hbar\mathbf{k} = \hbar\mathbf{k}' + \mathbf{p}_e}$

## B. The double-slit experiment with electrons: particles are waves

When small particles (electrons, $\alpha$-particles, or even $C_{60}$ 'bucky balls') are sent through small slits, they randomly change direction in violation to classical mechanics. Over many experimental runs, one can identify a probability $P(\mathbf{r})\,d\mathbf{r}$ that a particle arrives in a some small region $d\mathbf{r}$ around a point $\mathbf{r}$, and this probability looks similar to the intensity distribution of a diffracted wave.

This can be explained by de Broglie's phenomenological concept of 'matter waves'

$$\Psi(\mathbf{r}; t) = A\exp(i\mathbf{k} \cdot \mathbf{r} - i\omega t), \tag{1.6}$$

where the wave properties are related to the known kinetic properties of the particle in exactly the same manner as for the photons — the angular frequency is $\omega = E/\hbar$ and the wave vector is $\mathbf{k} = \mathbf{p}/\hbar$. The experimentally determined probability $P(\mathbf{r})$ is then found to be proportional to the intensity $|\Psi(\mathbf{r}; t)|^2$ of the matter wave. We call $\Psi(\mathbf{r}; t)$ the **wave function**.

### Points to remember

- All information about the state of a quantum mechanical system is encoded in a wave function, which in the examples above is of the form $\Psi(\mathbf{r}; t)$.

- The nature of this information is probabilistic. E.g., the probability density of a particle at position $\mathbf{r}$ is given by $P(\mathbf{r}) = |\Psi(\mathbf{r}; t)|^2$.

## II. THE SCHRÖDINGER EQUATION

We now introduce the central equation of quantum mechanics, the Schrödinger equation, which can be seen as a generalisation of the phenomenological explanations described above to situations where particles experience arbitrary forces. We also introduce the concept of *operators* related to *observables* (measurable properties such as momentum and energy).

### A. Wave equation for photons

For simplicity consider a particle moving in one dimension, with position measured by a coordinate $x$. A freely propagating wave with wave number $k$ and angular frequency $\omega$ is described by

$$\Psi_k(x; t) = A\exp(ikx - i\omega t). \tag{2.1}$$

For light (photons), $\omega = kc$, and we know that $\Psi_k(x;t)$ solves the wave equation

$$\frac{\partial^2 \Psi(x;t)}{\partial t^2} = c^2 \frac{\partial^2 \Psi(x;t)}{\partial x^2}. \qquad (2.2)$$

Indeed, if we insert $\Psi(x;t) = \Psi_k(x;t)$ into this equation it reduces to

$$-\omega^2 \Psi_k(x;t) = -c^2 k^2 \Psi_k(x;t). \qquad (2.3)$$

Let us multiply the left-hand side of Eq. (2.3) with $(i\hbar)^2 = -\hbar^2$, and the right-hand side with $(-i\hbar)^2 = -\hbar^2$. With the help of the Planck and de Broglie relations, we then find (check that both forms are indeed identical!)

$$E^2 \Psi_k(x;t) = c^2 p^2 \Psi_k(x;t). \qquad (2.4)$$

For arbitrary $\Psi(x;t)$, we now repeat this manipulation for the wave equation (2.2) itself:

$$\left(i\hbar \frac{\partial}{\partial t}\right)^2 \Psi(x;t) = c^2 \left(-i\hbar \frac{\partial}{\partial x}\right)^2 \Psi(x;t). \qquad (2.5)$$

This reformulation turns out to be very convenient. Notice that the operations

$$i\hbar \frac{\partial}{\partial t} \Psi_k(x;t) = E \Psi_k(x;t), \qquad (2.6)$$

$$-i\hbar \frac{\partial}{\partial x} \Psi_k(x;t) = p \Psi_k(x;t), \qquad (2.7)$$

allow us to directly read off the energy and momentum of the photons with wavefunction (2.1). If $\Psi(x;t)$ is not of the specific form $\Psi_k(x;t)$, the result of these operations is not just a multiplication with a number ($E$ or $p$). However, if we define

$$i\hbar \frac{\partial}{\partial t} \Psi(x;t) \equiv \hat{E} \Psi(x;t), \qquad (2.8)$$

$$-i\hbar \frac{\partial}{\partial x} \Psi(x;t) \equiv \hat{p} \Psi(x;t), \qquad (2.9)$$

the result always fulfils the wave equation

$$\hat{E}^2 \Psi(x;t) = c^2 \hat{p}^2 \Psi(x;t). \qquad (2.10)$$

Notice the similarity to Eq. (2.4). We call $\hat{E}$ the **energy operator** and $\hat{p}$ the **momentum operator**. The mathematical properties of these operators are explored later on in this course.

### Points to remember

- Physical observables are associated with operators.

- Momentum operator $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$, $\hat{p}_y = -i\hbar \frac{\partial}{\partial y}$, $\hat{p}_z = -i\hbar \frac{\partial}{\partial z}$;

- Energy operator $\hat{E} = i\hbar \frac{\partial}{\partial t}$.

- Position operator $\hat{x} = x$, $\hat{y} = y$, $\hat{z} = z$.

- E.g.:
  $\hat{p}_x \hat{x} f(x) = -i\hbar \frac{d}{dx}(xf(x))$
  $\hat{x}\hat{p}_x f(x) = -xi\hbar \frac{d}{dx}(f(x))$.

## B. The Schrödinger equation

For light, we have $\hat{E}^2 \Psi(x;t) = c^2 \hat{p}^2 \Psi(x;t)$ in *correspondence* to the relation $E^2 = c^2 p^2$ for energy and momentum of the photons. This correspondence shall guide as a heuristic principle from classical mechanics to quantum mechanics.

For particles with finite mass (at non-relativistic speed), the total energy is given by $E = p^2/2m + V(x)$, where $T = p^2/2m = mv^2/2$ is the kinetic energy and $V(x)$ is the potential energy (recall that the force acting on the particle is $F(x) = -dV/dx$).

Reading the *correspondence principle* given above backwards, one finds the **Schrödinger equation**

$$\hat{E}\Psi(x;t) = \frac{\hat{p}^2}{2m} \Psi(x;t) + \hat{V}\Psi(x;t). \qquad (2.11)$$

Let us decode this equation and express it in usual mathematical notation:

$$i\hbar \frac{\partial \Psi(x;t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x;t)}{\partial x^2} + V(x)\Psi(x;t). \qquad (2.12)$$

In the steps above we associate to the potential energy an operator $\hat{V}$, which changes $\Psi(x;t)$ into

$$\hat{V}\Psi(x;t) \equiv V(x)\Psi(x;t). \qquad (2.13)$$

It is only consequent to also introduce the **position operator**

$$\hat{x}\Psi(x;t) \equiv x\Psi(x;t) \qquad (2.14)$$

and the operator of kinetic energy $\hat{T} \equiv \hat{p}^2/2m$. The combination

$$\hat{H} \equiv \hat{T} + \hat{V} = \hat{p}^2/2m + \hat{V} \qquad (2.15)$$

is called the **Hamilton operator** (or **Hamiltonian**), which is of central importance in quantum mechanics. It corresponds to the total energy in classical mechanics.

We now can restate the Schrödinger equation in the compact form

$$i\hbar \frac{\partial}{\partial t} \Psi(x;t) = \hat{H}\Psi(x;t). \qquad (2.16)$$

Even more compactly we can write

$$\hat{E}\Psi = \hat{H}\Psi, \qquad (2.17)$$

where we suppressed the arguments.

### Points to remember

- The evolution of the wave function (=state of the system) for a quantum particle of mass $m$ moving in one dimension is determined by the Schrödinger equation

$$i\hbar\frac{\partial\Psi(x;t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x;t)}{\partial x^2} + V(x)\Psi(x;t), \quad (2.18)$$

or

$$\hat{E}\Psi(x;t) = \hat{H}\Psi(x;t), \quad (2.19)$$

where $\hat{H} = \hat{p}^2/2m + \hat{V}(x)$ is the Hamiltonian.

## C. Stationary Schrödinger equation

If $\hat{H}$ does not explicitly depend on time [a counter example would be a driven particle sitting in a modulated potential $V(x;t)$], energy is classically conserved. In quantum mechanics, this results in a simplification of the Schrödinger equation, since we can separate out the time variable $t$. Let us write

$$\Psi_E(x;t) = \exp(-iEt/\hbar)\psi(x), \quad (2.20)$$

where the time dependence $\propto \exp(-iEt/\hbar) = \exp(-i\omega t)$ is the same as for a propagating plane wave, but the spatial dependence has not been specified yet. With the energy operator defined in Eq. (2.8), we then have $\hat{E}\Psi_E(x;t) = E\Psi_E(x;t)$ [see Eq. (2.6)]. It now remains to find an equation for the spatial dependence $\psi(x)$. We insert $\Psi_E(x;t)$ into the time-dependent Schrödinger equation (2.16) and obtain

$$E\psi(x)\exp(-iEt/\hbar) = \hat{H}\psi(x)\exp(-iEt/\hbar). \quad (2.21)$$

Divide by the time-dependent factor $\exp(-iEt/\hbar)$, and we end up with the **stationary Schrödinger equation**

$$E\psi(x) = \hat{H}\psi(x), \quad (2.22)$$

where $E$ is now just a real number. This equation is independent of time. For a particle of mass $m$ moving in a one-dimensional potential $V(x)$, its explicit form is

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x). \quad (2.23)$$

*This is the most important equation in this module, and we will study it for a wide range of problems. Hence, remember it well!*

### *Points to remember*

- For a particle of mass $m$ moving in one dimension, the states with fixed energy $E$ are determined by the stationary Schrödinger equation

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x). \quad (2.24)$$

## III. MATHEMATICAL INTERPRETATION OF THE SCHRÖDINGER EQUATION

### A. The Schrödinger equation as a differential equation

We can write the stationary Schrödinger equation (2.23) as

$$E\psi(x) = -\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x), \quad (3.1)$$

where $\psi''(x)$ denotes the second derivative of the wave function. Equation (3.1) is a homogeneous linear ordinary differential equation of second order. The solutions $\psi(x)$ have the following properties:

**Mathematical property I: superposition principle:** If $\psi_1(x)$ and $\psi_2(x)$ are solutions of Eq. (3.1) and $A$, $B$ are constants, then

$$\psi(x) = A\psi_1(x) + B\psi_2(x) \quad (3.2)$$

is also a solution of Eq. (3.1). This is a consequence of the linearity of Eq. (3.1).

**Mathematical property II: continuity conditions:** Any solution $\psi(x)$ is a continuous function (the function is smooth, i.e., has no jumps). The first derivative $\psi'(x)$ is also continuous, with the possible exception of points where $|V(x)| = \infty$. At such points, $\psi'(x)$ may jump, which translates into a 'kink' in $\psi(x)$ [i.e., $\psi(x)$ is still continuous, but suddenly changes its slope].

**Mathematical property III: boundary conditions**: The wave function must be bounded for $|x| \to \infty$ (i.e., it is not allowed to increase indefinitely). This condition has a physical origin, since if it were violated we could not interpret $|\psi(x)|^2$ as the position probability density (the particle would be sitting at $\pm\infty$).

### B. The Schrödinger equation as an eigenvalue problem

In general, $\psi(x)$ is a function, and $\hat{H}\psi(x)$ is just another function, which usually is of a very different form than $\psi(x)$. In solving the stationary Schrödinger equation, we find functions $\psi_n(x)$ such that $\hat{H}\psi_n = E_n\psi_n$. Thus, for a solution $\psi_n$ of the stationary Schrödinger equation the operation with $\hat{H}$ is equivalent to the multiplication by a real number $E_n$. Functions $\psi_n(x)$ with this property are called **eigenfunctions** of $\hat{H}$, and the numbers $E_n$ are known as **eigenvalues**. Informed by the physical meaning of these mathematical objects, the eigenfunctions of the Hamiltonian are also called **eigenstates**, and since the Hamiltonian represents energy its eigenvalues are called **eigenenergies**.

## C. Momentum eigenfunctions

Eigenfunctions and eigenvalues can also be defined for other operators $\hat{A}$, by requiring $\hat{A}\psi = a\psi$. In particular, the eigenfunctions of the momentum operator $\hat{p} = -i\hbar d/dx$ are

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} \exp(ipx/\hbar), \qquad (3.3)$$

and thus are given by the position-dependent part of the plane waves $\Psi_k$ [see Eq. (2.7); the stated form expresses $k$ by the eigenvalue $p$, and the stated amplitude ensures the appropriate normalisation of the probability distribution of momentum, introduced in Section VII.A].

## D. Position eigenfunctions and the Dirac delta-function

The eigenfunctions of $\hat{x}$ must be very localised in space, at some place $x_0$, and zero at all other places, so that $\hat{x}\psi_{x_0}(x) = x\psi_{x_0}(x) = x_0\psi_{x_0}(x)$. These highly singular functions can be expressed in terms of *Dirac's $\delta$-function*,

$$\psi_{x_0}(x) = \delta(x - x_0). \qquad (3.4)$$

The $\delta$-function is so singular that it actually does not constitute a proper function, but a so-called *distribution*. Its defining property is the following integral:

$$\int_{-\infty}^{\infty} dx f(x)\delta(x - x_0) = f(x_0) \qquad (3.5)$$

for any function $f(x)$ that is continuous at $x_0$. The $\delta$-function is real and symmetric, $\delta^*(x - x') = \delta(x - x') = \delta(x' - x)$.

### *Points to remember*

- The stationary Schrödinger equation is a linear differential equation, and the ensuing superposition principle, continuity requirements and boundary conditions determine important features of its solutions.

- The stationary Schrödinger equation can also be interpreted as an eigenvalue equation of the Hamiltonian, $\hat{H}\psi = E\psi$.

- The eigenfunctions of the momentum operator are given by $\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} \exp(ipx/\hbar)$.

## IV. A FIRST EXAMPLE: PARTICLE IN THE SQUARE WELL

## A. The particle in the one-dimensional square well

The Schrödinger equation involves the potential energy $V(x)$, which depends on the physical circumstances and may be arbitrarily complicated. A simple situation is a particle that bounces between two hard walls at $x = -L/2$ and $x = L/2$. This problem is called the particle in the box, or the particle in the square well, and is one of the few cases where the stationary Schrödinger equation can be solved explicitly.

Classically, at a given energy $E$ the particle bounces between the walls with velocity $v = \sqrt{2E/m}$ when the particle moves to the right and $v = -\sqrt{2E/m}$ when it moves to the left. The corresponding potential energy is given by

$$V(x) = 0 \quad \text{for } -\frac{L}{2} < x < \frac{L}{2},$$
$$V(x) = \infty \quad \text{elsewhere (in the walls).} \qquad (4.1)$$

You may wish to draw the potential on a piece of paper.

Because the walls are infinitely high, we don't expect to find the particle there at any time. This indeed follows from the stationary Schrödinger equation. In the walls, we have $E\psi(x) = (\hat{p}^2/2m + \infty)\psi(x) = \infty \times \psi(x)$, which (for finite energy $E$) only can be fulfilled for

$$\psi(x) = 0 \quad \text{for } x < -\frac{L}{2} \text{ or } x > \frac{L}{2}. \qquad (4.2)$$

Between the walls, the stationary Schrödinger equation has the simple form

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} \quad \text{for } -\frac{L}{2} < x < \frac{L}{2}. \qquad (4.3)$$

Even though in this notation it may look unfamiliar, this is just the wave equation for a vibrating string clamped between the walls (think of a guitar string, and see Young & Freedman chpt. 15.8.) The solutions are of the form

$$\psi(x) = a\cos kx + b\sin kx, \quad \text{where } k = \sqrt{2mE}/\hbar. \qquad (4.4)$$

This is a periodic function of $x$, with period (wave length) $\lambda = 2\pi/k$. However, not all values of $k$ are

allowed, since the wave function must match continuously (smoothly) with the solution $\psi = 0$ in the walls—the wavefunction cannot jump because this would correspond to an infinitely large kinetic energy (the kinetic energy is proportional to the second derivative of the wave function, see section II.B). This translates into the boundary conditions

$$\psi(-L/2) = 0, \qquad \psi(L/2) = 0. \qquad (4.5)$$

They can only be fulfilled simultaneously if the distance $\lambda/2 = \pi/k$ between the zeros of the oscillatory function Eq. (4.4) is a multiple of $L$, so that we can start with a zero at $x = -L/2$ and end up with another zero at $x = L/2$. The allowed values for $k$ hence are restricted to the discrete values

$$k_n = \frac{n\pi}{L}, \quad n \text{ an integer}. \qquad (4.6)$$

We say that $k$ is *quantised*. Since $k = \sqrt{2mE}/\hbar$, this translates directly into a **quantisation of the energy**,

$$E_n = \frac{k_n^2 \hbar^2}{2m} = \frac{\pi^2 \hbar^2}{2mL^2} n^2. \qquad (4.7)$$

The quantised energy values are also called **energy levels**.

Note that these values depend on the assumed form of the potential energy $V(x)$; changing the potential results in a different Schrödinger equation, which has different solutions and leads to other energies. We will get acquainted with this by studying several more examples, including the hydrogen atom. In general, the level with the lowest energy characterises the **ground state** of the system. In difference to classical mechanics, the ground-state energy is not equal to the minimal potential energy $V_{\min}$, corresponding to the classical particle at rest. (For the square well, $V_{\min} = 0$.) The difference $E_1 - V_{\min}$ is called **zero-point energy**, and we will later see that it can be explained by Heisenberg's uncertainty relation.

Based on the boundary conditions, you can confirm that the wave functions associated with the energy levels are

$$\psi_n = a_n \cos k_n x \quad \text{for } n \text{ odd}, \qquad (4.8)$$
$$\psi_n = b_n \sin k_n x \quad \text{for } n \text{ even}. \qquad (4.9)$$

We restrict $n$ to be positive, since negative values do not deliver independent solutions.

You find diagrams of the energy levels and the associated wave functions of the particle in the square well in almost every book on quantum mechanics (e.g., Young and Freedman, Fig. 40.4; A Rae, Fig 2.1). You could sketch them by yourself!

### Points to remember

- For a particle in an infinite square well of width $L$, the stationary Schrödinger equation in the region between the walls is given by

$$E\psi = -\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2}. \qquad (4.10)$$

This is solved by $\psi = a \cos kx + b \sin kx$ provided $E = \hbar^2 k^2 / 2m$.

- At the infinitely high walls, the wave function has to vanish ($\psi(x = \text{wall}) = 0$). This selects $k_n = n\pi/L$, where $n$ is an integer.

- The associated energies are $E_n = \frac{\pi^2 \hbar^2}{2mL^2} n^2$.

### B. Discussion: The probability interpretation of the wave function

Based on the specific solutions for the particle in the square well, we now can work to get a better feeling about the physical content of the wave function. What we already have agreed upon is to interpret

$$P(x) = |\psi(x)|^2 \qquad (4.11)$$

as the **probability density** in a position measurement. We say density, because in order to get an actual probability to find the particle in some interval $x_1 < x < x_2$ we still have to do an integral

$$P(x_1 < x < x_2) = \int_{x_1}^{x_2} dx\, P(x) = \int_{x_1}^{x_2} dx\, |\psi(x)|^2. \qquad (4.12)$$

If we do a position measurement, we would find the particle randomly located at various places, but after many experiments we would find the probability density as given in Eq. (4.11). We say the particle is **delocalised in space**. [Next to the wave functions for the first few levels of the particle in the square well, you may wish to sketch the corresponding probability densities $P(x)$.]

Since we will find the particle somewhere, we have to require

$$P(-\infty < x < \infty) = \int_{-\infty}^{\infty} dx\, P(x) = 1 \quad (4.13)$$

$$\Rightarrow \int_{-\infty}^{\infty} dx\, |\psi(x)|^2 = 1. \quad (4.14)$$

This is called the **normalisation condition** for the wave function, and must be obeyed for any wave function $\psi(x)$ representing the state of a quantum-mechanical particle in a one-dimensional potential.

For the square well, the normalisation condition delivers suitable values of the constants $a_n$, $b_n$ in Eqs. (4.8,4.9). For $n$ odd, the normalisation integral is given by

$$\int_{-L/2}^{L/2} dx |a_n|^2 \cos^2 \frac{\pi n x}{L} = |a_n|^2 \frac{L}{2}. \quad (4.15)$$

The normalisation condition hence is fulfilled for $a_n = \sqrt{2/L}$ (this is the most convenient choice), and the normalised wave function in $-L/2 < x < L/2$ is

$$\psi_n(x) = \sqrt{\frac{2}{L}} \cos \frac{\pi n x}{L} \quad \text{for } n \text{ odd}, \quad (4.16)$$

$$\psi_n(x) = \qquad\qquad \text{for } n \text{ even}. \quad (4.17)$$

(Exercise: fill in the result for $n$ even.)

### Points to remember

- (recall) The probability density to find a particle at position $x$ is $P(x) = |\psi(x)|^2$.

- The probability to find the particle between two positions $x_1$ and $x_2$ is given by

$$P(x_1 < x < x_2) = \int_{x_1}^{x_2} dx\, |\psi(x)|^2. \quad (4.18)$$

- The probability density has to be normalised: $\int_{-\infty}^{\infty} P(x)dx = 1$, hence $\int_{-\infty}^{\infty} |\psi(x)|^2\, dx = 1$. This is also called the normalisation condition of the wave function.

### C. Momentum and energy

What if instead of position we measure some other observable quantity of the particle in the square well, say its momentum or its energy?

Let's start with momentum. Recall that classically the particle bounces between the walls with constant velocity. This translates to the values for momentum $p = \sqrt{2mE}$ when the particle moves right and $p = -\sqrt{2mE}$ when the particle moves left. Also recall that in the case of the freely moving particle with the wave function $\Psi_k$ given in Eq. (2.1), we could read off the momentum from Eq. (2.7), $\hat{p}\Psi_k = p\Psi_k$.

For the particle in the box, we cannot read off the momentum in this way since the wave function $\hat{p}\psi_n$ is not proportional to $\psi_n$. E.g., for $n$ odd

$$-i\hbar \frac{d}{dx} \cos k_n x = i\hbar k_n \sin k_n x. \quad (4.19)$$

Indeed note that

$$\cos k_n x = \frac{1}{2}[\exp(ik_n x) + \exp(-ik_n x)] \quad (4.20)$$

is a **superposition** (sum) of wave functions that describe the particle moving right and left **at the same time**. So, the particle must be said to be **delocalised in momentum**. (Later we describe how to determine the probability that the particle has a given momentum $p$.)

On the other hand, the *energy* $E_n$ of the states $\psi_n$ fulfilling $\hat{H}\psi_n = E_n\psi_n$ is well defined. In reality, subsequent energy measurements on particles prepared in a state $\psi_n$ all would yield the same value $E_n$, so that for such a state there is no uncertainty attached to energy.

### Points to remember

- Values of observables are not certain. A quantum particle can have finite probabilities to be at different places, and move into different directions, all at the same time. A classical particle is certainly not capable of showing such a weird behavior.

## V. FURTHER EXAMPLES: BOUND STATES, EXTENDED STATES, AND TUNNELING

### A. Constant potential

Consider that the particle moves in a constant potential $V(x) = V_I$. It may be a good idea to sketch the potential on a piece of paper.

Classically, the total energy of the particle would

be given by $E = p^2/2m + V_I$. Part of the total energy is taken up by the potential energy $V_I$. The remaining kinetic energy is $p^2/2m = (E - V_I)$. We can solve for $p$ and find that the classical particle has momentum

$$p = \pm\sqrt{2m(E - V_I)}. \qquad (5.1)$$

Classically, no energies $E < V_I$ are allowed, since the momentum has to be real.

Quantum-mechanically, the particle is described by a wave function $\psi(x)$ which solves the Schrödinger equation

$$E\psi(x) = -\frac{\hbar^2}{2m}\psi''(x) + V_I\psi(x). \qquad (5.2)$$

It is useful to rearrange this equation by subtracting on both sides $V_I\psi(x)$. Then we obtain

$$(E - V_I)\psi(x) = -\frac{\hbar^2}{2m}\psi''(x). \qquad (5.3)$$

This is a *homogenous linear ordinary differential equation of second order with constant coefficients*. Its general solution is of the form

$$\psi(x) = A\exp(ikx) + B\exp(-ikx), \qquad (5.4)$$

where $A$ and $B$ are arbitrary complex numbers. The wave number $k$ is also a constant, and is found by inserting $\psi(x)$ into the Schrödinger equation:

$$(E - V_I)[A\exp(ikx) + B\exp(-ikx)]$$
$$= \frac{\hbar^2 k^2}{2m}[A\exp(ikx) + B\exp(-ikx)]. \qquad (5.5)$$

This gives the condition $(E - V_I) = \frac{\hbar^2 k^2}{2m}$, which is satisfied for

$$k = \frac{\sqrt{2m(E - V_I)}}{\hbar}. \qquad (5.6)$$

Note that this is of the form $k = |p|/\hbar$, where $p$ is the classical momentum (5.1). (This is just the de Broglie relation for momentum.) A second solution is $k = -|p|/\hbar$, but we have already taken care of it by the second exponential in (5.4). For $E > V_I$ (the classically allowed case), $k$ is positive, and the solution $\psi(x)$ is the superposition of a plane wave that moves to the right (amplitude $A$) and a plane wave that moves to the left (amplitude $B$). If we would make an experiment that measures the direction of the particle, we would find the probabilities for motion into each direction as

$$P(\text{particle moves right}) = \frac{|A|^2}{|A|^2 + |B|^2}, \qquad (5.7)$$

$$P(\text{particle moves left}) = \frac{|B|^2}{|A|^2 + |B|^2}. \qquad (5.8)$$

(We could normalise the wave function to $|A|^2 + |B|^2 = 1$ to obtain simpler expressions, but here it is useful to keep the discussion more general.)

We can also find solutions for $E < V_I$. The wave number $k$ is then imaginary,

$$k = \frac{\sqrt{2m(E - V_I)}}{\hbar} = i\frac{\sqrt{2m(V_I - E)}}{\hbar} \equiv i\kappa, \qquad (5.9)$$

where we introduced the real number $\kappa = \frac{\sqrt{2m(V_I - E)}}{\hbar}$. The wave function is then of the form

$$\psi(x) = A\exp(-\kappa x) + B\exp(\kappa x). \qquad (5.10)$$

The first term increases rapidly for $x \to -\infty$, and the second term increases rapidly for $x \to \infty$. According to the mathematical property III listed in Sec. III.A, we have to discard these solutions. Our only choice is to set $A = B = 0$. Hence, just as in the classical case, the particle cannot have energy $E < V_I$.

### Points to remember

- Probabilities of momentum can be read off by decomposing the wave function into a superposition of plane waves.

- The energy of a quantum particle is bounded from below by the minimum of the potential energy of a system.

### B. Constant potential, terminated by a hard wall

A hard wall is a region in space where $V(x) = \infty$. Let us consider the potential

$$V(x) = \begin{cases} V_I & \text{for } x < 0 \\ \infty & \text{for } x > 0 \end{cases}, \qquad (5.11)$$

which is constant for $x < 0$ and represents a hard wall for $x > 0$.

For simplicity, let us assume that $V_I = 0$.

Classically, the particle moves with momentum $p = \sqrt{2mE}$ to the right, bounces from the hard

wall at $x = 0$, and then moves with momentum $p = -\sqrt{2mE}$ to the left.

For $x > 0$, the Schrödinger equation is of the form $E\psi(x) = \infty\psi(x)$, which only can be fulfilled for $\psi(x) = 0$. Hence, just as in the classical case, the particle is never found in the hard wall.

For $x < 0$, the Schrödinger equation is just of the same form as in the previous section, Eq. (5.3), with $V_I = 0$. The general solution is again of the form Eq. (5.4), but now we have to take care of the *mathematical property II* listed in Sec. III.A: the wave function has to be continuous at $x = 0$. Since in the wall $\psi(x) = 0$, we have to require that

$$\psi(0) = A + B = 0. \qquad (5.12)$$

Hence, $B = -A$, and the wave function becomes

$$\psi(x) = A\exp(ikx) - A\exp(-ikx) = 2Ai\sin kx \quad \text{for } x < 0. \qquad (5.13)$$

Compared to the previous section, we hence have 'lost' one free coefficient in the wave function. This is the consequence of the boundary condition $\psi(x) = 0$ at the hard wall. Since $|B|^2 = |A|^2$, the probability to find the particle moving to the right is equal to the probability to find the particle moving to the left.

## C. Constant potential, terminated by a soft wall

A soft wall is a region in space where $V(x) = V_{II}$ is constant and larger than the potential in the bordering regions. Let us consider the potential

$$V(x) = \begin{cases} 0 & \text{for } x < 0 \\ V_{II} > 0 & \text{for } x > 0 \end{cases}, \qquad (5.14)$$

which represents a soft wall in the region $x > 0$.

Classically, a soft wall serves the same purpose (namely, being a wall) as a hard wall as long as the total energy $E < V_{II}$. Just as in case of the hard wall, the particle moves with momentum $p = \sqrt{2mE}$ to the right, bounces from the soft

wall at $x = 0$, and then moves with momentum $p = -\sqrt{2mE}$ to the left.

We call $x < 0$ the 'region I' and $x > 0$ the 'region II', and denote the wave function in each region by $\psi_I$ and $\psi_{II}$, respectively.

In region II ($x > 0$), the Schrödinger equation is given by

$$E\psi_{II}(x) = -(\hbar^2/2m)\psi_{II}''(x) + V_{II}\psi_{II}(x), \qquad (5.15)$$

which is of the same form as Eq. (5.3) but with $V_I$ replaced by $V_{II}$. Since we assume $E < V_{II}$, the solutions are of the form given in Eq. (5.10),

$$\psi_{II}(x) = A_{II}\exp(-\kappa_{II}x) + B_{II}\exp(\kappa_{II}x), \qquad (5.16)$$

where $\kappa_{II} = \frac{1}{\hbar}\sqrt{2m(V_{II} - E)}$. When we first encountered this solution, we ruled it out completely, since it was increasing over all bounds for $x \to \pm\infty$. Now, however, we are only concerned with the behaviour for $x > 0$. Hence, we only can conclude that $B_{II} = 0$, since the other part of the solution (with coefficient) decays rapidly to 0 for $x \to \infty$. Thus, we have

$$\psi_{II}(x) = A_{II}\exp(-\kappa x) \quad \text{for } x > 0. \qquad (5.17)$$

For $x < 0$, the Schrödinger equation is also of the form of Eq. (5.3), but with $V_I = 0$. The general solution is given in Eq. (5.4), so that

$$\psi_I(x) = A_I\exp(ik_Ix) + B_I\exp(-ik_Ix), \quad k_I = \frac{1}{\hbar}\sqrt{2mE}. \qquad (5.18)$$

Now we have to join the two regions I and II together. This procedure is called *wave matching*, and again is based on the continuity requirements (*mathematical property II* above). First of all, the wave function has to be continuous at $x = 0$. This gives

$$\psi_I(0) = \psi_{II}(0), \qquad (5.19)$$
$$A_I + B_I = A_{II}. \qquad (5.20)$$

Moreover, since the potential is finite, the first derivative of the wave function has to be continuous as well:

$$\psi_I'(0) = \psi_{II}'(0), \qquad (5.21)$$
$$ik(A_I - B_I) = -\kappa A_{II}. \qquad (5.22)$$

We have two conditions (5.20), (5.22), for three coefficients $A_I$, $B_I$, and $A_{II}$. So, we may choose $A_I$ as a given parameter and express the $B_I$ and $A_{II}$ in terms of it. This results in

$$ik(A_I - B_I) = -\kappa(A_I + B_I) \Rightarrow B_I = \frac{ik + \kappa}{ik - \kappa}A_I \qquad (5.23)$$

and

$$A_{II} = A_I + B_I \Rightarrow A_{II} = \frac{2ik}{ik - \kappa} A_I. \quad (5.24)$$

Just as in the previous section, we only have one free coefficient in the wave function, $A_I$. In region I, the particle is described by the wave function $\psi_I$. Since $|B_I|^2 = |A_I|^2$ (please check!), the probability to find the particle moving to the right is still equal to the probability to find the particle moving to the left. In region $II$, the particle is described by the wave function $\psi_{II}$.

From our solution we find that $A_{II}$ is finite, hence, $\psi_{II}(x)$ does *not* vanish in the classically forbidden region II. This physical phenomenon is known as **tunnelling into classically forbidden regions**. A quantum particle can be found in regions of space which are energetically forbidden for a classical particle. One also says that the particle *tunnels* into the classically forbidden region.

### D. Tunnelling through a potential barrier

In order to illustrate the dramatic consequences of tunnelling, consider the potential

$$V(x) = \begin{cases} 0 & \text{for } x < 0 \quad \text{(region I)} \\ V_0 > 0 & \text{for } 0 < x < L \quad \text{(region II)} \\ 0 & \text{for } x > L \quad \text{(region III)} \end{cases},$$
$$(5.25)$$

which represents a potential barrier of height $V$ and length $L$. For $E < V_0$, a classical particle arriving from the left (region I) would be reflected at the soft wall at $x = 0$ and could never enter region III.

In order to find the quantum-mechanical solution of this problem, first observe that the potential is constant in each of the three regions, so that we can readily write down the separate solutions of the Schrödinger equation,

$$\psi_I(x) = A_I e^{ikx} + B_I e^{-ikx} \quad (5.26)$$
$$\psi_{II}(x) = A_{II} e^{-\kappa x} + B_{II} e^{\kappa x} \quad (5.27)$$
$$\psi_{III}(x) = A_{III} e^{ikx} + B_{III} e^{-ikx}, \quad (5.28)$$

where $k = \frac{1}{\hbar}\sqrt{2mE}$ and $\kappa = \frac{1}{\hbar}\sqrt{2m(V_0 - E)}$.

The amplitudes $A_I$ and $B_{III}$ describe incoming particles from the left and right, respectively. The amplitudes $B_I$ and $A_{III}$ describe outgoing particles. As mentioned above, we assume that the particle initially arrives from the left, described by the amplitude $A_I$, but does not arrive from the right. This requires us to set $B_{III} = 0$. The amplitude $B_I$ describes the case that the particle is *reflected* from the barrier, while $A_{III}$ describes the case that the particle is *transmitted*. The probabilities $R$ of

reflection and $T$ of transmission are given by

$$R = \frac{|B_I|^2}{|A_I|^2}, \quad T = \frac{|A_{III}|^2}{|A_I|^2}. \quad (5.29)$$

In order to calculate these probabilities, we again use continuity (the *mathematical property II*) and find four conditions for the five coefficients (setting $B_{III} = 0$ as just discussed):

$$\psi_I(0) = \psi_{II}(0) \Rightarrow A_I + B_I = A_{II} + B_{II}$$
$$\psi_I'(0) = \psi_{II}'(0) \Rightarrow ik(A_I - B_I) = -\kappa(A_{II} - B_{II})$$
$$\psi_{II}(L) = \psi_{III}(L) \Rightarrow A_{II}e^{-\kappa L} + B_{II}e^{\kappa L} = A_{III}e^{ikL}$$
$$\psi_{II}'(L) = \psi_{III}'(L)$$
$$\Rightarrow -\kappa(A_{II}e^{-\kappa L} - B_{II}e^{\kappa L}) = ikA_{III}e^{ikL}. \quad (5.30)$$

This linear system of equations can be solved (e.g. by Gaussian elimination) in order to express all coefficients by the amplitude $A_I$ of the incoming particle. In particular, one finds the slightly unwieldy expression

$$A_{III} = A_I \frac{4ik\kappa \exp(-ikL)}{(\kappa + ik)^2 \exp(-\kappa L) - (\kappa - ik)^2 \exp(\kappa L)}.$$
$$(5.31)$$

The transmission probability can be written as

$$T = \frac{|A_{III}|^2}{|A_I|^2} \quad (5.32)$$

$$= \frac{4k^2\kappa^2}{4k^2\kappa^2 + (k^2 + \kappa^2)\sinh^2(\kappa L)} \quad (5.33)$$

$$= \frac{4E(V_0 - E)}{4E(V_0 - E) + V_0^2 \sinh^2(\kappa L)}. \quad (5.34)$$

Here $\sinh(x) = \frac{1}{2}(e^x - e^{-x})$ is the hyperbolic sine function. Since $T > 0$ we have to conclude that there is a finite probability that the particle *tunnels* through the wall.

For along barrier with $\kappa L \gg 1$, we can use that $\sinh x \sim e^x/2 \gg 1$ for $x \to \infty$, and simplify

$$T = \frac{16E(V_0 - E)}{V_0^2} e^{-2\kappa L}. \quad (5.35)$$

Hence, the tunnel probability becomes very small for long (macroscopic) barriers. The probability is also very small for a very high wall ($V_0 \gg E$).

This physical phenomenon is known as **tunnelling through a classically forbidden region**. A quantum particle can penetrate walls, especially if they are short and energetically not too high.

For the problems discussed so far in this chapter, the particle can always escape to $x = -\infty$, and in some cases also to $x = +\infty$. Solutions of this type are called **extended states**. They cannot be normalised (the integral $\int_{-\infty}^{\infty} |\psi(x)|^2 dx$ diverges), but still permit a probabilistic interpretation for

the momentum (propagation direction) of the particle. The energy of extended states can be changed continuously. This is contrast to the energy of a particle in a square well, which we discussed in the preceding chapter and briefly revisit in the following section.

### E. Two hard walls

This is identical to the particle in the square well (see section IV). There, we encountered a type of solution which is generally known as **bound states**. This describes a quantum particle which is confined in a potential well (so that it cannot escape to $x = \pm\infty$). The associated states are normalisable. Importantly, bound-state solutions of the Schrödinger equation can only be found for discrete (*quantised*) values of energy.

As mentioned before, the lowest bound state is called the ground state. Classically, the energy is minimised when the particle rests in the minimum of the potential. The quantum-mechanical ground-state energy, however, is elevated above this classical minimum by the zero-point energy. For the particle in the square well, the zero point energy is $E_1 = \frac{\pi^2\hbar^2}{2mL^2}$. Later we will see that this is due to the fact that a quantum particle can never be at rest at a fixed position, a restriction which is captured by Heisenberg's uncertainty principle.

### F. General classification of states

The distinction of bound states and extended states can be carried over to general one-dimensional potentials with arbitrary position dependence. Generally, one finds:

- bound states at energies where the particle cannot escape to infinity. Only discrete values of the energy are allowed. The wavefunction can be normalised.

- extended states at energies where the particle can escape to infinity (including escape by tunneling). A continuous range of energies is allowed.

### VI. THE HARMONIC OSCILLATOR

In quantum mechanics, the harmonic oscillator is an important paradigm because it provides a model for a variety of systems, such as the modes of the electrodynamic field (photons) and the vibrations of molecules and solids (phonons).

### A. Classical harmonic oscillator

The classical harmonic oscillator describes a particle subject to a restoring force $F = -m\omega^2 x$ proportional to the distance from an equilibrium position $x = 0$. Newton's equation $m\ddot{x} = F$ results in an oscillatory motion $x(t) = x_0 \cos\omega t + (v_0/\omega)\sin\omega t$, where $\omega = 2\pi/T$ and $T$ is the oscillation period. In this solution, $x_0 = x(0)$ is the initial position and $v_0 = \dot{x}(0)$ is the initial velocity of the particle. According to $F = -V'$, the force $F = -m\omega^2 x$ corresponds to a parabolic potential energy

$$V(x) = \frac{1}{2}m\omega^2 x^2. \tag{6.1}$$

### B. Schrödinger equation of the quantum harmonic oscillator

In order to solve this problem quantum mechanically, we follow our standard steps. The Schrödinger equation of the harmonic oscillator is given by

$$E\psi(x) = -\frac{\hbar^2}{2m}\psi''(x) + \frac{1}{2}m\omega^2 x^2\psi(x). \tag{6.2}$$

This equation is again a linear differential equation of second order, but now one coefficient is position dependent. From our general considerations we already can anticipate the following:

- The solutions $\psi(x)$ are continuous.

- The derivatives $\psi'(x)$ of the solutions are also continuous.

- As $V(x) \to \infty$ for $|x| \to \infty$, the particle cannot escape to infinity at finite energy $E$. This only permits bound states, which decay $\psi(x) \to 0$ as $|x| \to \infty$.

- The energies of the bound states are discrete (i.e., only at certain energies we can find valid solutions of the Schrödinger equation).

- The ground state energy $E_0$ will be larger than the classical minimal energy: $E_0 > 0$.

### C. Mathematical solution

Let us first focus on finding the mathematical solutions of the Schrödinger equation. We start by bringing the Schrödinger equation into a simpler, rescaled form. Denote $\psi(x) = \varphi(x\sqrt{m\omega/\hbar})$, which corresponds to a rescaled position $y = x\sqrt{m\omega/\hbar}$.

According to the chain rule, $\psi' = \sqrt{m\omega/\hbar}\varphi'$ and $\psi'' = (m\omega/\hbar)\varphi''$. We also write energy as $E = \frac{\hbar\omega}{2}\epsilon$. In terms of $\varphi$, the Schrödinger equation then reads

$$\frac{\hbar\omega}{2}\epsilon\varphi(y) = -\frac{\hbar\omega}{2}\varphi''(y) + \frac{\hbar\omega}{2}y^2\varphi(y), \qquad (6.3)$$

or, after cancelling the common factor $\frac{\hbar\omega}{2}$,

$$\epsilon\varphi(y) = -\varphi''(y) + y^2\varphi(y). \qquad (6.4)$$

Next, we introduce the new function $\varphi(y) = e^{-y^2/2}f(y)$. By applying the product rule, we then find the following standard differential equation:

$$\epsilon f = -f'' + 2yf' + f. \qquad (6.5)$$

When $\varepsilon \neq 2n + 1$, where $n = 0, 1, 2, \ldots$ is an integer, the solutions of Equation (6.5) grow rapidly for $|y| \to \infty$, even outgrowing the factor $\exp(-y^2/2)$ appearing in $\varphi(y) = e^{-y^2/2}f(y)$. These solutions do not fulfil our boundary conditions for $|x| \to \infty$ and hence have to be discarded.

For $\varepsilon = 2n + 1$, $n = 0, 1, 2, \ldots$, however, Eq. (6.5) has simple solutions $f(y) = H_n(y)$ which are just polynomials of degree $n$. These polynomials are known as the *Hermite polynomials*. The first two of these polynomials are simply $H_0 = 1$ and $H_1 = 2y$. The other polynomials can be calculated recursively, $H_{n+1}(y) = 2yH_n(y) - 2nH_{n-1}(y)$.

### D. Ground state and first excited state

The first two solutions correspond to the ground state and the first excited state of the harmonic oscillator:

**Ground state**: $n = 0$, $f = 1$, which gives to $f' = f'' = 0$. This is a solution of Eq. (6.5) if $\epsilon = 1$, which corresponds to an energy $E_0 = \frac{1}{2}\hbar\omega$. The wave function is given by

$$\psi_0(x) = c_0 \exp\left(-x^2\frac{m\omega}{2\hbar}\right),$$

where $c_0$ can be determined from the normalisation condition $\int_{-\infty}^{\infty} |\psi(x)|^2\,dx = 1$ (see below). This gives $c_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$.

**First excited state**: $n = 1$, $f = 2y$, hence $f' = 2$ and $f'' = 0$. This is a solution of Eq. (6.5) if $\epsilon = 3$, which corresponds to $E_1 = \frac{3}{2}\hbar\omega$. The wave function is given by

$$\psi_1(x) = c_1 x \exp\left(-x^2\frac{m\omega}{2\hbar}\right),$$

with normalisation constant $c_1 = \left(4\frac{m^3\omega^3}{\pi\hbar^3}\right)^{1/4}$.

### E. Normalisation of the ground state wave function

The ground state wave function of the harmonic oscillator provides us with a good occasion to practice once more the normalisation of the wave function. Since we want to interpret $|\psi_0(x)|^2 = P(x)$ as the probability density for position, we require

$$\int_{-\infty}^{\infty} |\psi_0(x)|^2\,dx = 1.$$

With $\psi_0(x) = c_0 \exp(-x^2\frac{m\omega}{2\hbar})$ this integral reads

$$\int_{-\infty}^{\infty} c_0^2 \exp\left(-x^2\frac{m\omega}{\hbar}\right)\,dx.$$

We use the standard integral $\int_{-\infty}^{\infty} \exp(-ax^2)\,dx = \sqrt{\pi/a}$, where we set $a = \frac{m\omega}{\hbar}$:

$$\int_{-\infty}^{\infty} c_0^2 \exp\left(-x^2\frac{m\omega}{\hbar}\right)\,dx = c_0^2\sqrt{\frac{\pi\hbar}{m\omega}}.$$

The equates to 1 if $c_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$, in agreement with the value given in the previous section.

### F. General form of the bound states

In general, the normalised bound-state wave functions are given by

$$\psi_n = C_n H_n(x\alpha)e^{-x^2\alpha^2/2}, \qquad (6.6)$$

$n = 0, 1, 2, 3, \ldots$, $C_n = \alpha^{1/2}\pi^{-1/4}(n!2^n)^{-1/2}$, where $\alpha = \sqrt{\frac{m\omega}{\hbar}}$.

The associated bound-state energies are

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, \ldots. \qquad (6.7)$$

Note that the *difference* between two consecutive energies is given by Planck's relation $E = \hbar\omega$.

You could now draw diagrams of the potential, bound state energies, ground- and excited state wave functions, and the associated probability densities of the particle position.

## VII. MOMENTUM PROBABILITIES AND THE UNCERTAINTY PRINCIPLE

So far we have a quantitative prescription to obtain the probability density to find a particle somewhere in space: $P(x) = |\psi(x)|^2$. In this section we introduce probabilities of momentum and describe how they are related to position probabilities. This culminates in the celebrated Heisenberg uncertainty principle.

## A. Momentum wave function

In analogy to the case of position $x$, we can introduce a momentum wave function $\tilde{\psi}(p)$, which delivers the probability to find the value $p$ in a momentum measurement as $P(p) = |\tilde{\psi}(p)|^2$. This momentum wave function is given by

$$\tilde{\psi}(p) = (2\pi\hbar)^{-1/2} \int_{-\infty}^{\infty} \exp(-ipx/\hbar)\psi(x)\,dx. \quad (7.1)$$

Mathematically, this is known as the *Fourier transformation* of $\psi(x)$ and simply decomposes $\psi(x)$ into plane waves $\exp(ipx/\hbar)$. Note that such plane waves are eigenfunction of the momentum operator, $\hat{p}\exp(ipx/\hbar) = p\exp(ipx/\hbar)$. The Fourier transform in Eq. (7.1) involves the complex conjugate $\exp(-ipx/\hbar)$ of this function. The factor $(2\pi\hbar)^{-1/2}$ ensures that the resulting probability density of momentum $P(p) = |\tilde{\psi}(p)|^2$ is properly normalised. In other words, we can write Eq. (7.1) also as

$$\tilde{\psi}(p) = \int_{-\infty}^{\infty} \psi_p^*(x)\psi(x)\,dx, \quad (7.2)$$

where $\psi_p(x)$ is the momentum eigenfunction given in (3.3).

Observe that according to Eq. (7.1), $\psi(x)$ and $\tilde{\psi}(p)$ are not independent of each other. Hence, $P(x)$ and $P(p)$ are also not independent of each other, which has direct physical consequences such as Heisenberg's uncertainty relation, to which we come shortly.

## B. Expectation values of position and momentum

The averaged result of many experiments measuring some observable $\hat{A}$ is called the *expectation value* of $\hat{A}$, denoted by $\langle A \rangle$. According to the general rules for probabilities, the expectation value is obtained from the probability density $P(A)$ by weighting it with the result $A$:

$$\langle A \rangle = \int A P(A)\,dA. \quad (7.3)$$

We can also calculated expectation values of functions of $A$, such as $A^2$:

$$\langle A^2 \rangle = \int A^2 P(A)\,dA. \quad (7.4)$$

Hence, the expectation value of position is

$$\langle x \rangle = \int x\,|\psi(x)|^2\,dx, \quad (7.5)$$

and the expectation value of position-squared is

$$\langle x^2 \rangle = \int x^2 |\psi(x)|^2\,dx. \quad (7.6)$$

The expectation values of momentum are given by $\langle p \rangle = \int p\,P(p)\,dp = \int p\,|\tilde{\psi}(p)|^2\,dp$, $\langle p^2 \rangle = \int p^2 P(p)\,dp = \int p^2\,|\tilde{\psi}(p)|^2\,dp$. Now, using standard theorems about the Fourier transformation (see PHYS213), one can express these expectation values directly in terms of the wave function $\psi(x)$:

$$\langle p \rangle = \int \psi^*(x)[\hat{p}\,\psi(x)]\,dx \quad (7.7)$$

$$= -i\hbar \int \psi^*(x)\psi'(x)\,dx, \quad (7.8)$$

$$\langle p^2 \rangle = \int \psi^*(x)[\hat{p}^2\,\psi(x)]\,dx \quad (7.9)$$

$$= -\hbar^2 \int \psi^*(x)\psi''(x)\,dx. \quad (7.10)$$

Hence, in order to calculate these expectation values one does not need to carry out a Fourier transformation; instead, one only needs to evaluate an ordinary integral.

## C. Uncertainty

A particularly useful quantity related to the expectation values is the standard deviation

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}. \quad (7.11)$$

In quantum mechanics, the standard deviation is known as the *uncertainty* of the observable $A$.

In simple situations, $P(A)$ is peaked around some value. The expectation value $\langle A \rangle$ then gives us an indication of the position of this peak, while $\Delta A$ gives us an indication of the width of this peak.

## D. Heisenberg's uncertainty relation

Using again standard theorems about the Fourier transformation (see PHYS213), a strongly peaked position wave function $\psi(x)$ corresponds to a very broad momentum wave function $\tilde{\psi}(p)$, and vice versa. Mathematically, this can be expressed as a relation for the uncertainties of momentum and position:

$$\Delta x \Delta p \geq \hbar/2. \quad (7.12)$$

This is the celebrated *Heisenberg uncertainty relation*. As a consequence, the better the position of a particle is determined, the less precisely determined is its momentum, and vice versa.

This relation also explains the zero-point energy of a particle in a potential, which we already have encountered for the particle in the square well.

Classically, the minimal total energy $E = V_{\min}$ is obtained when the particle rests at the minimum of the potential. A quantum-mechanical particle never can be at rest at a potential minimum, since then both its position (at the minimum) and its momentum (which vanishes at rest) would be fixed.

## E. Example I: Minimal-uncertainty wave packet

Minimal-uncertainty wave packets are states that satisfy Eq. (7.12) as an equality

$$\Delta x \Delta p = \frac{\hbar}{2} \qquad \text{(for minimal uncertainty).} \quad (7.13)$$

Their general form is

$$\psi(x) = (2\pi\sigma^2)^{-1/4} \exp\left[-\frac{(x-x_0)^2}{4\sigma^2} + \frac{i}{\hbar}p_0(x-x_0)\right], \quad (7.14)$$

where $x_0$, $p_0$, and $\sigma$ are real parameters.

The probability density $P(x) = |\psi(x)|^2$ associated with a minimal-uncertainty wave packet takes the form of a *normal distribution*

$$P(x) = |\psi(x)|^2 = (2\pi\sigma^2)^{-1/2} \exp[-(x-x_0)^2/2\sigma^2]. \quad (7.15)$$

The distribution is symmetric around $x_0$, hence $\langle \hat{x} \rangle = x_0$. The uncertainty is given by $\Delta x = \sigma$, and is independent of $x_0$.

The momentum wave function $\tilde{\psi}(p)$ is obtained via the Fourier transformation (7.1). The result is

$$\tilde{\psi}(p) = (\hbar^2\pi/2\sigma^2)^{-1/4} \exp\left[-\frac{\sigma^2(p-p_0)^2}{\hbar^2} - \frac{i}{\hbar}px_0\right], \quad (7.16)$$

which gives

$$P(p) = (\hbar^2\pi/2\sigma^2)^{-1/2} \exp\left[-2\sigma^2(p-p_0)^2/\hbar^2\right]. \quad (7.17)$$

This is again a normal distribution, shifted away from the origin by $\langle \hat{p} \rangle = p_0$. The widths can be read off by comparing to Eq. (7.15): $\sigma^2$ is replaced by $\hbar^2/4\sigma^2$. Hence $\Delta p = \frac{\hbar}{2\sigma}$, and the product of uncertainties $\Delta x \Delta p$ indeed satisfies Eq. (7.13).

Minimal-uncertainty wave packets have many applications, especially since they are the best approximation to the "classical" situation in which both the position and the momentum of a particle are specified at the same time. A prominent example of a minimal-uncertainty wave packet is the ground state of a harmonic oscillator, which is discussed on a worksheet.

## F. Example II: ground state of the particle in the square well

Let us now consider the ground state wave function of a particle in a square well with two hard walls at $x = \pm L/2$. This wave function is given by $\psi = \sqrt{\frac{2}{L}}\cos(\pi x/L)$ in between the walls, and vanishes inside the walls.

We find the expectation values $\langle x \rangle = 0$, $\langle p \rangle = 0$, $\langle x^2 \rangle = L^2(1/12 - 1/2\pi^2)$, and $\langle p^2 \rangle = \hbar^2\pi^2/L^2$. Hence $\Delta x \approx 0.181\,L$ and $\Delta p = \hbar\pi/L$, so that $\Delta x \Delta p \approx 0.57\hbar$, which clearly fulfils the uncertainty relation.

The maximal position uncertainty $\Delta x_{\max} = L/2$ is obtained for a particle that sits with equal probability at $x = \pm L/2$. Hence, the uncertainty in momentum in any state fulfils $\Delta p \geq \hbar/L$.

This can be used to give a lower bound for the ground state (or zero-point) energy: $E_1 = \langle p^2 \rangle/2m \geq (\Delta p)^2/2m \geq \frac{\hbar^2}{2mL^2}$. The exact result $E_1 = \frac{\hbar^2\pi^2}{2mL^2}$ clearly fulfills this condition.

## G. Energy-time uncertainty relation

In the Schrödinger equation, time is not an observable but a parameter. Hence, no operator is associated with time. However, it is still useful to talk about the duration of events in quantum mechanics. A good example is an atomic excitation, which decays over a certain time $\Delta t$. If one looks at the outgoing radiation, the frequency is not sharp but spread over a range $\Delta\omega \sim 1/\Delta t$ (you will verify this on a worksheet). In quantum mechanics, frequency is related to energy via $E = \hbar\omega$, and one ends up with the *energy-time uncertainty relation*

$$\Delta t \Delta E \geq \hbar/2. \quad (7.18)$$

The specific value $\hbar/2$ of the lower bound can be motivated from the similar forms of the energy and momentum operators $\hat{E} = i\hbar\frac{\partial}{\partial t}$ and $\hat{p} = -i\hbar\frac{\partial}{\partial x}$, which differ (besides the sign) only by the variable which they differentiate ($t$ or $x$).

Even though the energy-time uncertainty relation stands on a different footing than the position-momentum uncertainty relation, it is as useful as the latter. In many cases a quantum system is excited into a state of a finite lifetime. Fluorescent atoms are one example, radioactive nuclei another. In solids, charge carriers occupy the available states only with a finite lifetime because they are disturbed by disorder and interactions. In these systems, often a detailed calculation of the quantum dynamics is complicated, but the energy-time uncertainty relation captures many important effects.

## VIII. MATHEMATICAL INTERLUDE: HILBERT SPACES AND LINEAR OPERATORS

In the next chapter we will formulate the general principles of quantum mechanics. Here, we introduce the necessary mathematical framework, which concerns vectors, scalar products (a complex version of the dot product), and operators. We describe these entities in the powerful *Dirac notation*, which is widely used throughout quantum mechanics.

### A. Vectors

The most common form of a vector is a collection of components $\psi_n$, $n = 1, \ldots, \mathcal{N}$, where $\mathcal{N}$ denotes the dimension of the vector space. A function $\psi(x)$ can be consider as a vector in which the discrete index $n$ has been replaced by a continuous index $x$. It is useful to introduce a formalism in which this analogy can be exploited without direct reference to the specific forms of the components $\psi_n$ or $\psi(x)$.

In Dirac notation, vectors are denoted as $|\psi\rangle$. These vectors form a *complex linear vector space*, which entails the following properties: Any vector $|\psi\rangle$ can be scaled by any complex number $\alpha$, i.e., we can form new vectors $|\alpha\psi\rangle = \alpha|\psi\rangle$. Furthermore, any two vectors $|\psi\rangle$, $|\chi\rangle$ can be combined into new vectors by a forming a *superposition* $|\psi + \chi\rangle = |\psi\rangle + |\chi\rangle$. These operations obey the distributive law $(\alpha + \beta)(|\psi\rangle + |\chi\rangle) = |\alpha\psi\rangle + |\beta\psi\rangle + |\alpha\chi\rangle + |\beta\chi\rangle$. In addition, a vector space possesses a null vector $|\mathbb{0}\rangle$ such that $|\mathbb{0}\rangle + |\psi\rangle = |\psi\rangle$, and to each vector $|\psi\rangle$ there is an inverse vector $|-\psi\rangle = -|\psi\rangle$ such that $|\psi\rangle - |\psi\rangle = |\mathbb{0}\rangle$

These properties are all nicely fulfilled for functions. In particular, if $\psi(x)$ and $\chi(x)$ are functions and $\alpha$, $\beta$ are constants, then $\alpha\psi(x) + \beta\chi(x)$ is also a function.

### B. Scalar product, norm and orthogonality

The *scalar product* is a generalised versions of the dot product, which associates a complex number $\langle\psi|\chi\rangle$ to any pair of vectors $|\psi\rangle$, $|\chi\rangle$. The scalar product fulfils the important property

$$\langle\psi|\chi\rangle = \langle\chi|\psi\rangle^*. \tag{8.1}$$

Consistently with this, the scalar product is linear in the second argument, but *conjugate linear* in the first argument, i.e., $\langle\psi|\alpha\chi\rangle = \alpha\langle\psi|\chi\rangle$, $\langle\alpha\psi|\chi\rangle = \alpha^*\langle\psi|\chi\rangle$, $\langle\psi + \varphi|\chi\rangle = \langle\psi|\chi\rangle + \langle\varphi|\chi\rangle$, $\langle\psi|\varphi + \chi\rangle = \langle\psi|\varphi\rangle + \langle\psi|\chi\rangle$.

In general, a scalar product must be positive definite, $\langle\psi|\psi\rangle > 0$ for $|\psi\rangle \neq |\mathbb{0}\rangle$. We call $||\psi|| = \sqrt{\langle\psi|\psi\rangle}$ the *norm* of the vector $|\psi\rangle$ (this generalises the notion of length of an ordinary vector). A vector with $\langle\psi|\psi\rangle = 1$ is called *normalised* (this generalises the notion of a unit vector). The procedure of passing from a vector $|\psi\rangle$ to the normalised vector $(1/||\psi||)|\psi\rangle$ is called *normalisation*. Again in analogy to the case of ordinary vectors, two vectors $|\psi\rangle$, $|\chi\rangle$ fulfilling $\langle\psi|\chi\rangle = 0$ are said to be *orthogonal to each other*.

In conjunction with a certain completeness condition which is always fulfilled in quantum mechanics, a vector space equipped with a scalar product is called a *Hilbert space*.

Formally, the scalar product can be interpreted as a product $\langle\psi|\cdot|\chi\rangle$ between the vectors $|\chi\rangle$ and the entities $\langle\psi|$, which form the *dual vector space*. They represent the left entries in the scalar product and therefore are also conjugate linear: $\langle\alpha\psi + \beta\chi| = \alpha^*\langle\psi| + \beta^*\langle\chi|$. A dual vector is also called a *bra*, and an ordinary vector is called a *ket*, alluding to the fact that in the scalar product $\langle\psi|\chi\rangle$ they form a bracket (bra-ket). The introduction of these dual vectors is an important step in the Dirac notation; its usefulness will become clear when we discuss operators (generalised matrices).

### C. Basis

A *basis* is a collection of vectors $|n\rangle$, $n = 1, 2, 3, \ldots, \mathcal{N}$ such that any vector can be written as a superposition $|\psi\rangle = \sum_{n=1}^{\mathcal{N}} \psi_n|n\rangle$, where the complex coefficients $\psi_n$ are unique. The coefficients $\psi_n$ give a *representation* of the vector, and can be written as a column vector

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_{\mathcal{N}} \end{pmatrix}. \tag{8.2}$$

The corresponding dual vector is written as a row vector $\psi^\dagger = (\psi_1^*, \psi_2^*, \ldots, \psi_{\mathcal{N}}^*)$. While there are many possible bases, in which the same vector is represented by different coefficients, the number $\mathcal{N}$ of basis vectors required to obtain all vectors is always the same, and is called the *dimension* of the vector space ($\mathcal{N}$ may be $\infty$).

An orthogonal basis fulfills $\langle n|m\rangle = 0$ for any $n \neq m$. If furthermore $\langle n|n\rangle = 1$ for all $n$ one speaks of an *orthonormal basis*. In such a basis, the coefficients representing a vector are given by $\psi_n = \langle n|\psi\rangle$, and the scalar product takes the ex-

plicit form

$$\langle\psi|\chi\rangle = \sum_n \psi_n^* \chi_n = \psi^\dagger \chi. \qquad (8.3)$$

Thus, a vector $|\psi\rangle$ is normalised if its coefficients in an orthonormal basis obey

$$\sum_n |\psi_n|^2 = 1. \qquad (8.4)$$

For functions $\psi(x)$, the summation over the discrete index is replaced by an integration, $|\psi\rangle = \int \psi(x)|x\rangle\,dx$. In this case the dimension of the vector space is infinite. The orthonormality of a basis can be stated with help of the Dirac delta function, $\langle x|x'\rangle = \delta(x - x')$. In the scalar product, the summation over the discrete index $n = 1, 2, \ldots$ is again replaced by an integration over the continuous index $x$,

$$\langle\psi|\varphi\rangle = \int \psi^*(x)\varphi(x)\,dx. \qquad (8.5)$$

This type of integral is called an *overlap integral*. The expression for the expansion coefficients takes the form $\psi(x) = \langle x|\psi\rangle$, and the normalisation condition translates into

$$\int |\psi(x)|^2\,dx = 1.$$

## D. Linear operators

An operator $\hat{A}$ converts any vector $|\psi\rangle$ into another vector $|\hat{A}\psi\rangle = \hat{A}|\psi\rangle$. Linear operators fulfill $\hat{A}(\alpha|\psi\rangle + \beta|\chi\rangle) = \alpha\hat{A}|\psi\rangle + \beta\hat{A}|\chi\rangle$, where $\alpha$, $\beta$ are complex numbers. Operators can be added according to the rule $(\hat{A} + \hat{B})|\psi\rangle = \hat{A}|\psi\rangle + \hat{B}|\psi\rangle$, and multiplied according to the rule $(\hat{B}\hat{A})|\psi\rangle = \hat{B}(\hat{A}|\psi\rangle)$.

In Dirac notation, operators are written as $\hat{A} = \sum_{nm} A_{nm}|n\rangle\langle m|$, and the action of an operator is obtained from the multiplication rule $\langle m| \cdot |\psi\rangle = \langle m|\psi\rangle$. Thus,

$$\hat{A}|\psi\rangle = \sum_{nm} A_{nm}|n\rangle\langle m|\psi\rangle = \sum_n \left(\sum_m A_{nm}\langle m|\psi\rangle\right)|n\rangle. \qquad (8.6)$$

Assuming that the states $|n\rangle$, $|m\rangle$ in the definition of $\hat{A}$ form an orthonormal basis, the operator can be represented by $N \times N$-dimensional square matrices

$$A = \begin{pmatrix} A_{11} & A_{12} & \ldots & A_{1N} \\ A_{21} & A_{22} & \ldots & A_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ A_{N1} & A_{N2} & \ldots & A_{NN} \end{pmatrix} \qquad (8.7)$$

where, the *matrix elements* $A_{nm}$ are obtained from $A_{nm} = \langle n|\hat{A}m\rangle \equiv \langle n|\hat{A}|m\rangle$. Since in an orthonormal basis $\langle m|\psi\rangle = \psi_m$, the operator then acts on a vector according to the standard rules of matrix multiplication, i.e., $|\varphi\rangle = \hat{A}|\psi\rangle$ is represented by a vector with coefficients $\varphi_n = \sum_m A_{nm}\psi_m$. Furthermore, the operator addition and multiplication rules then translate to the usual prescriptions of matrix addition and multiplication.

## E. Eigenvalues and eigenvectors

The action of an operator is particularly simple in its *eigenrepresentation*, defined by a basis fulfilling the *eigenvalue equation* $\hat{A}|n\rangle = a_n|n\rangle$. The numbers $a_n$ are called *eigenvalues*, and the associated vectors $|n\rangle$ are called *eigenvectors*. When appropriate, these eigenvectors are also called *eigenfunctions*.

If the eigenvectors form an orthonormal basis (as is the case for the hermitian and unitary operators considered below), the eigenrepresentation results in a diagonal matrix, with $A_{nm} = 0$ if $n \neq m$ and $A_{nn} = a_n$. In Dirac notation, the operator can then be written as $\hat{A} = \sum_n a_n|n\rangle\langle n|$.

## F. Common types of operators

A particularly simple operator is the identity operator $\hat{I}$ which leaves all states unchanged, $\hat{I}|\psi\rangle = |\psi\rangle$. Every state is therefore an eigenstate of $\hat{I}$, with eigenvalue 1. Consequently, in any orthonormal basis this operator takes the same form $\hat{I} = \sum_n |n\rangle\langle n|$. Representations are simply obtained by multiplying out the identities $|\psi\rangle = \hat{I}|\psi\rangle$ and $\hat{A} = \hat{I}\hat{A}\hat{I}$. In a given orthonormal basis, it is useful to decompose the identity $\hat{I} = \sum \hat{P}_n$ as the sum of *projection operators* $\hat{P}_n = |n\rangle\langle n|$, which fulfill $\hat{P}_n\hat{P}_m = 0$ if $n \neq m$, and $\hat{P}_n^2 = \hat{P}_n$.

For each operator $\hat{A}$ we can define an *adjoint operator* $\hat{A}^\dagger$ by setting $\langle\psi|\hat{A}^\dagger\chi\rangle = \langle\hat{A}\psi|\chi\rangle$. In an orthonormal basis we then have $A_{nm}^\dagger = A_{mn}^*$. For many operators, we can also define an inverse operator $\hat{A}^{-1}$ which fulfils $\hat{A}\hat{A}^{-1} = \hat{I}$.

Two important types of operators are *hermitian* operators $\hat{H}$ and *unitary* operators $\hat{U}$. For any two states $|\psi\rangle$, $|\chi\rangle$, hermitian operator fulfill $\langle\psi|\hat{H}\chi\rangle = \langle\hat{H}\psi|\chi\rangle$, while unitary operators fulfill $\langle\hat{U}\psi|\hat{U}\chi\rangle = \langle\psi|\chi\rangle$. This entails $\hat{H} = \hat{H}^\dagger$ and $\hat{U}^\dagger = \hat{U}^{-1}$. In an orthonormal basis, the matrix elements of a hermitian operator fulfill $H_{nm} = H_{mn}^*$, while those of a unitary operator fulfill $\sum_l U_{nl}U_{ml}^* = \delta_{nl}$.

Both classes of operators have the nice property that their sets of normalised eigenvectors form an

orthonormal basis. For hermitian operators, the eigenvalues $a_n$ are real, while for unitary operators they fulfill $|a_n| = 1$.

Unitary operators are analogous to orthogonal matrices which rotate a coordinate system. In particular, any basis change from one orthonormal basis $|n\rangle$ to another orthonormal basis $|\tilde{n}\rangle$ can be written as $|\tilde{n}\rangle = \hat{U}|n\rangle$, where $\hat{U}$ is a suitable unitary operator. A common form of unitary operators relates them to a hermitian operator $\hat{H}$ via $\hat{U} = \exp(i\tau\hat{H})$, where $\tau$ is a real constant and the exponential of an operator is defined via its Taylor expansion, $\exp(\hat{A}) = \sum_{n=0}^{\infty} \hat{A}^n/n!$. In this case, $\hat{U}^{-1} = \hat{U}^\dagger = \exp(-i\tau\hat{H})$. Furthermore, the operators $\hat{H}$ and $\hat{U}$ then share the same eigenvectors: If $\hat{H} = \sum_n h_n|h_n\rangle\langle h_n|$, then $\hat{U} = \sum_n u_n|h_n\rangle\langle h_n|$ with eigenvalues $u_n = \exp(i\tau h_n)$.

## IX. GENERAL PRINCIPLES OF QUANTUM MECHANICS

We now have all the tools to formulate the general principles of quantum mechanics, which we state in terms of *four postulates*.

### A. Quantum states

*Postulate I:* All experimentally accessible information about a quantum system is contained in a state vector $|\psi\rangle$.

*Remarks:* An example is the wave function $\psi(x)$ of a point particle in one dimension. In three dimensions a point particle is described by a wave function $\psi(x, y, z)$. We will also discuss the state of two particles with position $\mathbf{r_1}$ and $\mathbf{r_2}$, which is described by a wave function $\psi(\mathbf{r_1}, \mathbf{r_2})$. Furthermore, we encounter the spin of an electron, which is described by a two-component vector $\psi = \binom{\psi_\uparrow}{\psi_\downarrow}$.

### B. Observables and operators

*Postulate II:* Each experimentally observable quantity $\hat{A}$ is represented by a *hermitian* linear operator.

*Remarks:* Here, the term *observable* refers to any measurable quantity. Examples are position $\hat{x} = x$, momentum $\hat{p} = -i\hbar\frac{d}{dx}$, energy $\hat{H} = \hat{p}^2/2m + V(x)$, but also kinetic energy $\hat{T} = \hat{p}^2/2m$ and potential energy $\hat{V} = V(x)$ can serve as observables. Another example is the angular momentum $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ in three-dimensional systems, where $\hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z})$ is a vector composed of the three position operators, and $\mathbf{p} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)$ is a vector composed of the three momentum operators $p_x = -i\hbar\frac{\partial}{\partial x}$, $p_y = -i\hbar\frac{\partial}{\partial y}$,

$p_z = -i\hbar\frac{\partial}{\partial z}$. Later we will also consider an analogous vector operator $\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$ representing the spin of an electron.

In the context of quantum mechanics, eigenvectors $|a_n\rangle$ of an observable $\hat{A}$ are also called *eigenstates*. The property of hermiticity ensures that all the eigenvalues $a_n$ are real, while the eigenstates can be used to construct an orthonormal basis.

### C. Dynamics

*Postulate III:* The time evolution $|\psi(t)\rangle$ of a quantum state is governed by the *Schrödinger equation*

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle, \qquad (9.1)$$

where $\hat{H}$ is a system-specific hermitian operator called *Hamiltonian*.

*Remarks:* In the particular case $\hat{H} = \mathrm{const}(t)$ of a time-independent Hamiltonian, the eigenvalues of $\hat{H}$ are denoted as $E_n$, and are interpreted as energies of solutions $|\psi(t)\rangle = \exp(-iE_n t/\hbar)|n\rangle$. Here, the stationary states $|n\rangle$ fulfill the eigenvalue equation $E_n|n\rangle = \hat{H}|n\rangle$, which is known as the stationary Schrödinger equation.

Given an initial state $|\psi(t_0)\rangle$, the general solution can always be written as $|\psi(t)\rangle = \hat{U}(t, t_0)|\psi(t_0)\rangle$, where $\hat{U}(t, t_0)$ is a unitary operator called the *time evolution operator*. This operator fulfills the Schrödinger equation $i\hbar\frac{d}{dt}\hat{U}(t, t_0) = \hat{H}(t)\hat{U}(t, t_0)$ with initial condition $\hat{U}(t_0, t_0) = \hat{I}$. For a time-independent Hamiltonian, the time evolution operator takes the explicit form

$$\hat{U}(t, t_0) = \exp[-i(t - t_0)\hat{H}/\hbar]. \qquad (9.2)$$

Using the eigenrepresentation $\hat{H} = \sum_n E_n|n\rangle\langle n|$ of the Hamiltonian we can write $\hat{U}(t, t_0) = \sum_n \exp[-i(t - t_0)E_n/\hbar]|n\rangle\langle n|$. We will examine time dependence in detail in later chapters.

### D. Measurements

The last postulate concerns the remarkable quantum effects which occur when one determines the value of an observable in an experiment. Since this is the most complicated postulate we break it down into three aspects.

#### 1. Experimentally observable values

*Postulate IVa:* In an experiment that determines the value $a$ of an observable with associated operator $\hat{A}$, the *only possible (allowed) observable values* are the *eigenvalues* $a_n$ of $\hat{A}$.

*Remarks:* E.g., when one measures the energy of a particle bound in a potential well, the only possible results are the discrete energies $E_n$ determined by the stationary Schrödinger equation. Because of the hermiticity constraint on such operators, these values are always real.

2. Generalised wave function and probability

*Postulate IVb:* If the normalised state of the system at the time of the measurement is $|\psi\rangle$, each outcome occurs with probability

$$P(a) = \sum_{a_n=a} |\langle n|\psi\rangle|^2 = \sum_{a_n=a} \langle\psi|\hat{P}_n|\psi\rangle, \qquad (9.3)$$

where $|n\rangle$ is the eigenstate associated with $a_n$, and $\hat{P}_n = |n\rangle\langle n|$ is the associated projection operator.

*Remarks:* Using the orthonormality of the eigenstates $|n\rangle$ and the normalisation condition $\langle\psi|\psi\rangle = 1$, it follows that the probability $P(a)$ is automatically normalised: $\sum_a P(a) = 1$ if $a$ is discrete, and $\int P(a)\,da = 1$ if $a$ is continuous.

Disregarding for the moment the possibility that eigenvalues are degenerate, it is useful to interpret the probability in terms of a generalised wave function

$$\psi_A(a_n) = \langle n|\psi\rangle, \qquad (9.4)$$

which consists of the coefficients of the wave function in the eigenbasis of $\hat{A}$,

$$|\psi\rangle = \sum_n \psi_A(a_n)|n\rangle. \qquad (9.5)$$

The probability $P(a)$ that an experiment returns the value $\hat{A} = a$ is then given by

$$P(a) = |\psi_A(a)|^2. \qquad (9.6)$$

In one dimension, the generalised wavefunction is given by the overlap integral

$$\psi_A(a_n) = \int \psi_n^*(x)\psi(x)\,dx. \qquad (9.7)$$

An example is the momentum wave function $\tilde{\psi}(p)$, discussed in section VII.A, which is calculated with help of the momentum eigenfunction $\psi_p(x) = (2\pi\hbar)^{-1/2}\exp(ipx/\hbar)\,dx$, and corresponds to a Fourier transformation. The factor $(2\pi\hbar)^{-1/2}$ provides that $P(p) = |\tilde{\psi}(p)|^2$ is properly normalised.

3. Effect of experiments on the system state

*Postulate IVc:* A measurement with outcome $a$ transforms the quantum state into the state

$$|\psi'\rangle = \sqrt{1/P(a)} \sum_{a_n=a} \hat{P}_n|\psi\rangle. \qquad (9.8)$$

*Remarks:* Using the decomposition (9.5) of the pre-measurement state $|\psi\rangle$ in the eigenbasis of the measured observable $\hat{A}$, the post-measurement state can be written as $|\psi'\rangle = \sqrt{1/P(a)} \sum_{a_n=a} \psi_A(a_n)|n\rangle$. Thus, only the components of the eigenstates with eigenvalue compatible to the measured outcome $a$ are retained, and the result is then normalised. It follows that $|\psi'\rangle$ is an eigenstate of $\hat{A}$. In the case that the eigenvalues are not degenerate, a measurement with outcome $a_n$ simply transforms the state of the system into the eigenstate $|n\rangle$.

## X. CONSEQUENCES OF THE MEASUREMENT POSTULATE

We now formulate some practical consequences of the measurement postulate which greatly simplify the characterisation of the measured results.

### A. Expectation values

We define the *expectation value* of an observable $A$ via $\langle A\rangle = \int aP(a)\,da$ (for a continuous observable) or $\langle A\rangle = \sum_a aP(a)$ (for a discrete observable). This represents the averaged outcome of many experiments on identically prepared quantum systems.

Inserting the expression (9.3) for the probability $P(a)$ and making use of the form $\hat{A} = \sum_n a_n|n\rangle\langle n|$ of the operator in the eigenrepresentation, we find the important result

$$\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle. \qquad (10.1)$$

This allows us to calculate an expectation value without determining all eigenfunctions and eigenvalues of $\hat{A}$. In particular, for a particle with wave function $\psi(x)$, the expectation value is given by

$$\langle A\rangle = \int \psi^*(x)[\hat{A}\psi(x)]\,dx. \qquad (10.2)$$

The expectation value

$$\langle A^m\rangle = \langle\psi|\hat{A}^m|\psi\rangle \qquad (10.3)$$

is known as the *mth moment* of $\hat{A}$. The *uncertainty* of an observable is defined as the root-mean square standard deviation

$$\Delta A = \sqrt{\langle A^2\rangle - \langle A\rangle^2}. \qquad (10.4)$$

### B. Consecutive measurements

When the system state is identical to an eigenstate $|n\rangle$ of $\hat{A}$, it follows from the orthonormality of

these states that $P(a) = 0$ vanishes for all $a \neq a_n$, while $P(a_n) = 1$. In this special case, the value of the observable is well defined, and $\Delta A = 0$. The final part $IVc$ of the measurement postulate asserts that this situation is realised right after a measurement. Therefore, in immediately repeated measurements of the same observable one will obtain a sequence of identical results. However, while the post-measurement state is an eigenstate of the measured observable, it is in general not an eigenstate of other relevant observables. Thus, if one consecutively measures the values of different observables one will in general obtain a random sequence of outcomes with finite probabilities. The following considerations provide a simple rule that quantifies these observations in terms of the uncertainties of the different observables.

## C. Commutator

For each pair of operators $\hat{A}^{(1)}$, $\hat{A}^{(2)}$ we can introduce a new operator, called the commutator, which is denoted by $[\hat{A}^{(1)}, \hat{A}^{(2)}]$. This operator is defined as

$$[\hat{A}^{(1)}, \hat{A}^{(2)}] = \hat{A}^{(1)}\hat{A}^{(2)} - \hat{A}^{(2)}\hat{A}^{(1)}. \tag{10.5}$$

In other words, the commutator is an operator which acts as

$$[\hat{A}^{(1)}, \hat{A}^{(2)}]\psi = \hat{A}^{(1)}\hat{A}^{(2)}\psi - \hat{A}^{(2)}\hat{A}^{(1)}\psi. \tag{10.6}$$

If $\hat{A}^{(1)}$ and $\hat{A}^{(2)}$ were numbers the commutator would clearly vanish. For operators, however, the order generally matters. For instance, applying the product rule one finds $\frac{d}{dx}(x\psi) = \psi + x\frac{d}{dx}(\psi)$. Since $\hat{p} = -i\hbar\frac{d}{dx}$ this gives

$$[\hat{x}, \hat{p}] = i\hbar,$$

which is the most important of all commutators.

For some operators, $[\hat{A}^{(1)}, \hat{A}^{(2)}] = 0$. One then say that the operators $\hat{A}^{(1)}$ and $\hat{A}^{(1)}$ *commute*. An example is found in three-dimensional systems: Since the momentum operators are defined by partial derivatives we have, e.g., $[\hat{x}, \hat{p}_y] = 0$.

The importance of the commutator results from the following mathematical theorem: if two operators commute (i.e., their commutator $[\hat{A}^{(1)}, \hat{A}^{(2)}] = 0$ vanishes) then the eigenstates of $\hat{A}^{(1)}$ are identical to the eigenstates of $\hat{A}^{(2)}$. This holds even though the eigenvalues $a_n^{(1)}$, $a_n^{(2)}$ of both operators are generally different. In the joint eigenbasis, the operators then read $\hat{A}^{(1)} = \sum_n a_n^{(1)}|n\rangle\langle n|$, $\hat{A}^{(2)} = \sum_n a_n^{(2)}|n\rangle\langle n|$.

## D. Generalised uncertainty principle

Heisenberg's uncertainty principle can be generalised to quantify the extent of incompatibility of two arbitrary observables $A^{(1)}$, $A^{(2)}$ in terms of their uncertainties $\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$:

$$\Delta A^{(1)} \Delta A^{(2)} \geq \frac{1}{2}\left|\langle[\hat{A}^{(1)}, \hat{A}^{(2)}]\rangle\right|. \tag{10.7}$$

This gives a lower bound for the product of uncertainties of two observables, and expresses this lower bound by the expectation value of their commutator. For momentum and position, $[\hat{x}, \hat{p}] = i\hbar$, which is just a constant. Therefore $\langle i\hbar \rangle = i\hbar$, and $|i\hbar| = \hbar$. This recovers the conventional uncertainty relation $\Delta x \Delta p \geq \hbar/2$.

## E. Simultaneous and incompatible variables

According to Heisenberg's uncertainty principle, for commuting observables we find

$$\Delta A^{(1)} \Delta A^{(2)} \geq 0. \tag{10.8}$$

But since the uncertainty of any observable $\hat{A}$ is never negative, $\Delta A \geq 0$, this uncertainty relation poses no restriction whatsoever.

Indeed, if the wave function of a system is identical to a joint eigenfunction of two commuting operators $\hat{A}^{(1)}$ and $\hat{A}^{(2)}$, then the values of these operators are *both* defined precisely. Because of this, observables with vanishing commutator are also called *simultaneous* variables. An example is the position $\hat{x}$ and the momentum $\hat{p}_y$, which can be both determined at the same time (the wave function $\psi(x, y)$ is then well localised in $x$ direction, while it looks like a plane wave in $y$ direction).

On the other hand, pairs of observables such as $\hat{x}$ and $\hat{p}_x$ which do not commute are called *incompatible*, as they cannot be both fixed at the same time.

We can also understand this difference by reconsidering the effects of consecutive measurements of two observables $\hat{A}^{(1)}$ and $\hat{A}^{(2)}$.

- If the observables commute, then the order of measurements does not affect the probabilities, which are both calculated with the same (joint) eigenstates $|n\rangle$. After the two experiments, the state of system is a joint eigenstate, in which both observables are well defined.

- If the two observables are incompatible, the order of measurements matters. This is because the generalised wave function of both

observables has to be calculated with different eigenstates. Moreover, the state of the system after the two experiments is an eigenfunction of the observable that has been measured last. In this state, only the second observable is well defined, but the first observable is not (so if one carries out a third experiment which measures again the first observable, one generally finds a *different* value than in the first measurement).

In this sense, a measurement of an observable destroys the information obtained in earlier measurements of incompatible observables, but does not destroy the information obtained in earlier measurements of simultaneous observables.

### F. Complete determination of a state by measurements

In many situations the values of one observable alone do not suffice to uniquely determine the state of a system. This occurs whenever eigenvalues are degenerate, and thus are associated with several eigenstates. In such situations the complete determination of a state requires to measure a larger set $\hat{A}^{(l)}$ of simultaneous observables that all commute with each other, $[\hat{A}^{(l)}, \hat{A}^{(m)}] = 0$. This property guarantees that one can find a joint eigenbasis for all of these observables, given by states $|\mathbf{a}\rangle = |a^{(1)}, a^{(2)}, a^{(3)}, \ldots\rangle$ fulfilling $\hat{A}^{(l)}|\mathbf{a}\rangle = a^{(l)}|\mathbf{a}\rangle$. These states are only fully specified by knowledge of the eigenvalues $a^{(l)}$ of the full set of simultaneous observables.

### XI. PERTURBATION THEORY

Perturbation theory is a general method to analyse complex quantum systems in terms of simpler variants. The method relies on the expectation values, matrix elements and overlap integrals just introduced, which we now use to break down complex quantum processes into simpler parts. We focus on the simplest version of the method, which results in simple systematic approximations of energy levels. For completeness we also present details of the derivation, which illustrates the power of the Dirac notation.

### A. Objective

We want to find approximations for the energies $E_n$ and eigenstates $|\psi_n\rangle$ of a Hamiltonian $\hat{H}$,

$$E_n|\psi_n\rangle = \hat{H}|\psi_n\rangle, \tag{11.1}$$

assuming that the Hamiltonian is of the form $\hat{H} = \hat{H}^{(0)} + \hat{w}$, where $\hat{H}^{(0)}$ represents a simplified system with energies $E_n^{(0)}$ and eigenstates $|\psi_n^{(0)}\rangle$ solving the Schrödinger equation

$$E_n^{(0)}|\psi_n^{(0)}\rangle = \hat{H}^{(0)}|\psi_n^{(0)}\rangle. \tag{11.2}$$

The difference $\hat{w} = \hat{H} - \hat{H}^{(0)}$ between the real and the simplified system is called the *perturbation*, and the approximation scheme is called *perturbation theory*.

### B. Method

The idea of perturbation theory is to assume that the perturbation $\hat{w} = \lambda\hat{W}$ is the product of an operator $\hat{W}$ and a *small* number $\lambda$ (determining the strength of the perturbation).

Since the Hamiltonian

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{W} \tag{11.3}$$

now depends on the parameter $\lambda$, the energies $E_n$ and eigenstates $|\psi_n\rangle$ also depend on this parameter.

Consequently, we can expand the energies and eigenstates into a series:

$$E_n(\lambda) = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$
$$= \sum_{l=0}^{\infty} \lambda^l E_n^{(l)}, \tag{11.4}$$
$$|\psi_n(\lambda)\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots$$
$$= \sum_{l=0}^{\infty} \lambda^l|\psi_n^{(l)}\rangle. \tag{11.5}$$

Perturbation theory provides a systematic scheme to express the quantities $E_n^{(l)}$ and $|\psi_n^{(l)}\rangle$ in terms of the unperturbed energies $E_n^{(0)}$, the unperturbed eigenstates $|\psi_n^{(0)}\rangle$, and the *matrix elements of the perturbation*

$$W_{mn} = \langle\psi_m^{(0)}|\hat{W}|\psi_n^{(0)}\rangle.$$

The scheme commences by introducing the series expansions (11.4) and (11.5) into the Schrödinger equation (11.1) and sorting the expressions

order by order in $\lambda$:

$$E_n^{(0)}|\psi_n^{(0)}\rangle +$$
$$\lambda(E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle) +$$
$$\lambda^2(E_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(2)}|\psi_n^{(0)}\rangle) +$$
$$\cdots$$
$$=$$
$$\hat{H}^{(0)}|\psi_n^{(0)}\rangle +$$
$$\lambda(\hat{H}^{(0)}|\psi_n^{(1)}\rangle + \hat{W}|\psi_n^{(0)}\rangle) +$$
$$\lambda^2(\hat{H}^{(0)}|\psi_n^{(2)}\rangle + \hat{W}|\psi_n^{(1)}\rangle) +$$
$$\cdots \qquad (11.6)$$

In order to fulfill this equation, the expressions in front of the powers $\lambda^l$ have to be identical on both sides of the equation.

Since we assume that the perturbation $\lambda$ is small, we concentrate on the first few orders.

**Zeroth order perturbation theory**:
In zeroth order of $\lambda$ (collecting all terms that are independent of $\lambda$) one finds

$$\lambda^0 : \quad E_n^{(0)}|\psi_n^{(0)}\rangle = \hat{H}^{(0)}|\psi_n^{(0)}\rangle. \qquad (11.7)$$

This equation is identical to the unperturbed Schrödinger equation (11.2) and hence verifies that we chose the correct leading coefficient in each series. This result had to be expected since for $\lambda = 0$ the Hamiltonian $\hat{H} = \hat{H}^{(0)}$ equals the unperturbed Hamiltonian. Therefore the energies $E_n(\lambda = 0) = E_n^{(0)}$ are equal to the unperturbed energies, and the eigenstates $|\psi_n(\lambda = 0)\rangle = |\psi_n^{(0)}\rangle$ are identical with the unperturbed eigenstates.

**First order perturbation theory**:
In first order of $\lambda$ (collecting all terms that are proportional to $\lambda$) one finds

$$\lambda^1 : \quad E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle = \hat{H}^{(0)}|\psi_n^{(1)}\rangle + \hat{W}|\psi_n^{(0)}\rangle. \qquad (11.8)$$

The coefficient $E_n^{(1)}$ and the state $|\psi_n^{(1)}\rangle$ can now be determined using the orthonormality of the unperturbed eigenstates $|\psi_n^{(0)}\rangle$, i.e., $\langle\psi_m^{(0)}|\psi_n^{(0)}\rangle = \delta_{nm}$, where $\delta_{nm} = 1$ if $n = m$ and $\delta_{nm} = 0$ if $n \neq m$.

In order to use this property, take the scalar product of an unperturbed eigenstate $|\psi_m^{(0)}\rangle$ with both sides of Eq. (11.8):

$$E_n^{(0)}\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}\delta_{nm} = E_m^{(0)}\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle + W_{mn}. \qquad (11.9)$$

Here we used $\langle\psi_m^{(0)}|\hat{H}^{(0)}\psi_n^{(1)}\rangle = \langle\hat{H}^{(0)}\psi_m^{(0)}|\psi_n^{(1)}\rangle = E_m^{(0)}\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle$ and the definition of the matrix element $W_{mn}$.

For $n = m$, Eq. (11.9) reduces to

$$E_n^{(1)} = W_{nn}, \qquad (11.10)$$

while for $n \neq m$ we find

$$\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle = \frac{W_{mn}}{E_n^{(0)} - E_m^{(0)}}. \qquad (11.11)$$

Since the unperturbed eigenstates form a complete basis this gives

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{W_{mn}}{E_n^{(0)} - E_m^{(0)}}|\psi_m^{(0)}\rangle, \qquad (11.12)$$

where the sum is over all indices $m$, with the exception of $m = n$.

**Second order perturbation theory**:
By similar steps, one derives in the second order of $\lambda$

$$E_n^{(2)} = \sum_{m\neq n} \frac{|W_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}. \qquad (11.13)$$

In this course, we will not need $|\psi_n^{(2)}\rangle$, $E_n^{(3)}$, or higher terms of the perturbation series.

## C. Summary of the result

- Perturbed energy in first order of $\lambda$:

$$E_n \approx E_n^{(0)} + \lambda W_{nn}. \qquad (11.14)$$

  Hence, the energy shift $E_n - E_n^{(0)} = \lambda\langle\psi_n^{(0)}|\hat{W}|\psi_n^{(0)}\rangle = \langle\hat{w}\rangle$ is given by the expectation value of the perturbation $\hat{w}$.

- Perturbed eigenstate in first order of $\lambda$:

$$|\psi_n\rangle \approx |\psi_n^{(0)}\rangle + \lambda\sum_{m\neq n} \frac{W_{mn}}{E_n^{(0)} - E_m^{(0)}}|\psi_m^{(0)}\rangle. \qquad (11.15)$$

- Perturbed energy in second order of $\lambda$:

$$E_n \approx E_n^{(0)} + \lambda W_{nn} + \lambda^2\sum_{m\neq n} \frac{|W_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}. \qquad (11.16)$$

In the following we only need these results, not any details of their derivation.

## D. Example I: worn out harmonic oscillator

We now discuss various simple examples of perturbed systems, including cases where we can compare to exact solutions. The first example is a worn-out oscillator, described by a reduced restoring force $F = -m\omega_0^2 x + \lambda x$. This corresponds to a potential $V = \frac{1}{2}m\omega_0^2 x^2 - \frac{1}{2}\lambda x^2$, which is still parabolic, and hence still describes a harmonic oscillator.

**Exact solution:** The new oscillation frequency can be calculated from the curvature of the potential, $m\omega^2 = m\omega_0^2 - \lambda$, hence $\omega = \sqrt{\omega_0^2 - \lambda/m}$. This determines the exact perturbed energies

$$E_n = \hbar\omega(n + \frac{1}{2}). \qquad (11.17)$$

For small $\lambda$, the perturbed frequency can be approximated as

$$\omega \approx \omega_0 - \frac{\lambda}{2m\omega_0}. \qquad (11.18)$$

We focus on the ground state, with $n = 0$. The perturbed ground state energy can be approximated as

$$E_0 \approx \frac{1}{2}\hbar\omega_0 - \frac{\hbar\lambda}{4m\omega_0}. \qquad (11.19)$$

The first term is the unperturbed ground-state energy $E_0^{(0)} = \hbar\omega_0/2$. Consequently, the energy shift of the ground state is

$$E_0 - E_0^{(0)} \approx -\frac{\hbar\lambda}{4m\omega_0}. \qquad (11.20)$$

**Perturbation theory:** Let us see whether we can recover this result in perturbation theory.

The Hamiltonian

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega_0^2 x^2 - \frac{1}{2}\lambda x^2 \qquad (11.21)$$

differs from the unperturbed harmonic oscillator by the perturbation $\hat{w} = -\frac{1}{2}\lambda x^2$. According to first-order perturbation theory, the energy shift of the states is given by the expectation value of this perturbation, calculated with the unperturbed states. Hence, the ground-state energy shift is

$$E_0 - E_0^{(0)} \approx \langle\psi_0^{(0)}|\hat{w}|\psi_0^{(0)}\rangle = -\frac{1}{2}\lambda\langle\psi_0^{(0)}|\hat{x}^2|\psi_0^{(0)}\rangle, \qquad (11.22)$$

where $\psi_0^{(0)}(x) = \left(\frac{m\omega_0}{\pi\hbar}\right)^{1/4}\exp\left(-x^2\frac{m\omega_0}{2\hbar}\right)$ is the ground state wave function of the unperturbed harmonic oscillator (see section VI). This state has the form of a minimal-uncertainty wave packet (see section VII.E), for which we already obtained $\langle\psi_0^{(0)}|\hat{x}^2|\psi_0^{(0)}\rangle = \frac{\hbar}{2m\omega_0}$. Consequently, first-order perturbation theory predicts

$$E_0 - E_0^{(0)} \approx -\frac{1}{2}\lambda\frac{\hbar}{2m\omega_0}, \qquad (11.23)$$

which indeed agrees with Eq. (11.20).

## E. Example II: harmonic oscillator exposed to a constant force

Another exactly solvable perturbed problem describes a harmonic oscillator subjected to an additional constant force of strength $\lambda$, $F = -m\omega^2 x + \lambda$. A constant force simply shifts the equilibrium position (the position where the force vanishes) to

$$x_0 = \lambda/(m\omega^2). \qquad (11.24)$$

The potential energy can be written as

$$V(x) = \frac{1}{2}m\omega^2 x^2 - \lambda x, \qquad (11.25)$$

hence, the perturbation is $\hat{w} = -\lambda x$.
**Exact solution:** The potential energy can be written so that the new equilibrium position becomes apparent,

$$V(x) = \frac{1}{2}m\omega^2(x - x_0)^2 - \frac{1}{2}m\omega^2 x_0^2. \qquad (11.26)$$

This describes again a harmonic oscillator with the same frequency $\omega$ as before, but oscillating around $x = x_0$. The states $\psi_n(x) = \psi_n^{(0)}(x - x_0)$ hence are also simply shifted by $x_0$. We can now introduce a new coordinate $y = x - x_0$, and recover the potential energy of the unperturbed harmonic oscillator. The only difference the term

$$-\frac{1}{2}m\omega^2 x_0^2 = -\frac{\lambda^2}{2m\omega^2} \qquad (11.27)$$

which shifts the bound state energies to a lower value:

$$E_n - E_n^{(0)} = -\frac{\lambda^2}{2m\omega^2}. \qquad (11.28)$$

This result is exact. Notice that the shift is proportional to the square $\lambda^2$.
**Perturbation theory:** Let us see again whether we can recover this result in perturbation theory. Since the exact energy shift is proportional to the square of the perturbation strength we have to resort to second-order perturbation theory.

We again concentrate on the ground-state energy $E_0$. The first-order energy shift $E_0 - E_0^{(0)} \approx \lambda W_{00}$ is given by the expectation value of the perturbation $\hat{W} = -\hat{x}$,

$$W_{00} = -\langle\psi_0^{(0)}|\hat{x}|\psi_0^{(0)}\rangle. \qquad (11.29)$$

Now notice that $x\psi_0^{(0)}(x) = \sqrt{\hbar/(2m\omega)}\psi_1^{(0)}(x)$ is proportional to the wave function

$$\psi_1^{(0)}(x) = c_1 x \exp\left(-x^2\frac{m\omega}{2\hbar}\right),$$

of the first excited state of the unperturbed system, calculated in section VI.

Hence

$$W_{00} = -\langle\psi_0^{(0)}|x|\psi_0^{(0)}\rangle = -\sqrt{\hbar/(2m\omega)}\langle\psi_0^{(0)}|\psi_1^{(0)}\rangle = 0$$
(11.30)

due to the orthogonality of the eigenstates $|\psi_0^{(0)}\rangle$ and $|\psi_1^{(0)}\rangle$. This agrees with the absence of a term linear in $\lambda$ in the exact expression (11.28) of the energy shift.

In second-order perturbation theory,

$$E_0 \approx E_0^{(0)} + \lambda W_{00} + \lambda^2 \sum_{m\neq n} \frac{|W_{m0}|^2}{E_0^{(0)} - E_m^{(0)}}, \quad (11.31)$$

we have to calculate the matrix elements

$$W_{m0} = \langle\psi_m^{(0)}|\hat{W}|\psi_0^{(0)}\rangle \quad (11.32)$$
$$= -\langle\psi_m^{(0)}|\hat{x}|\psi_0^{(0)}\rangle \quad (11.33)$$
$$= -\sqrt{\hbar/(2m\omega)}\langle\psi_m^{(0)}|\psi_1^{(0)}\rangle \quad (11.34)$$

Again because of the orthogonality of the eigenstates $|\psi_n^{(0)}\rangle$, all of these matrix elements vanish, with the exception of the element

$$W_{10} = -\sqrt{\hbar/(2m\omega)}. \quad (11.35)$$

Hence the energy shift reduces to

$$E_0 - E_0^{(0)} \approx \frac{|W_{10}|^2}{E_0^{(0)} - E_1^{(0)}}. \quad (11.36)$$

Moreover, since $E_n^{(0)} = \hbar\omega(n+1/2)$, we have $E_0^{(0)} - E_1^{(0)} = -\hbar\omega$. Collecting all results we obtain

$$E_0 - E_0^{(0)} \approx \lambda^2 \frac{\hbar/(2m\omega)}{-\hbar\omega} = -\frac{\lambda^2}{2m\omega^2}, \quad (11.37)$$

which agrees with the exact result (11.28).

## F. Example III: anharmonic oscillator

The parabolic potential $V_{osc}(x) = \frac{1}{2}m\omega^2 x^2$ is often used as an approximation of the motion in around an equilibrium position $x - x_0$, such as in the vibration of molecules or solids. The exact potential $V(x)$ can be expanded in a Taylor series around the equilibrium position,

$$V(x) = V_0 + \frac{1}{2}m\omega^2(x-x_0)^2$$
$$+\text{terms of order } (x-x_0)^3 \text{ and higher.}$$
(11.38)

In this expansion there are no terms linear in $(x - x_0)$ since the force $F = -V'$ vanishes at the equilibrium position $x = x_0$.

As we have seen in example II, the constant $V_0$ simply shifts the energy, and the displacement by $x_0$ does not change the energies at all. In the following we set $x_0 = 0$, $V_0 = 0$.

The terms of order $x^3$ and higher are called the *anharmonicity* of the potential. Classically, they perturb the motion of the oscillator so that the oscillation period $T$ depends on the energy of the oscillator (recall the period $T$ of a harmonic oscillator is independent of the oscillation amplitude $\Delta x$). Quantum mechanical, this results in a perturbation of the bound-state energies. For small energies, the classical oscillation amplitude $\Delta x$ is small, and hence the effect of the anharmonic terms $x^n \propto \Delta x^n$ should be small and rapidly decrease with $n$. We hence only account for the anharmonic term of lowest order in the Taylor series,

$$V(x) = \frac{1}{2}m\omega^2 x^2 + \lambda\frac{x^n}{n!} \quad (11.39)$$

where typically $n = 3$, but sometimes also $n = 4$ or larger due to symmetries of the problem.

Now we apply perturbation theory in order to estimate the resulting energy shift of the ground state.

In first-order perturbation theory, the energy shift is given by the expectation value of the perturbation $\lambda x^n/n!$,

$$E_0 - E_0^{(0)} = \frac{\lambda}{n!}\langle\psi_0^{(0)}|x^n|\psi_0^{(0)}\rangle. \quad (11.40)$$

We hence have to calculate the overlap integral

$$\langle\psi_0^{(0)}|x^n|\psi_0^{(0)}\rangle = \int_{-\infty}^{\infty} x^n|\psi_0^{(0)}(x)|^2\,dx \quad (11.41)$$
$$= \int_{-\infty}^{\infty} x^n \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \exp\left(-x^2\frac{m\omega}{\hbar}\right)\,dx. \quad (11.42)$$

This integral *vanishes* if $n$ is an odd integer, since the integrand is antisymmetric (the integral from $-\infty$ to 0 exactly cancels the integral from 0 to $\infty$). Hence, in first-order perturbation theory

$$E_0 - E_0^{(0)} \approx 0 \quad (n \text{ odd}). \quad (11.43)$$

An energy shift is only found in second-order perturbation theory, which we however do not pursue for the present problem.

For $n$ and even integer we use the standard integral

$$\int_{-\infty}^{\infty} x^n \exp(-ax^2)\,dx = \sqrt{\pi}a^{-(n+1)/2}2^{-n}\frac{n!}{(n/2)!},$$

where we set $a = \frac{m\omega}{\hbar}$. This gives the first order energy shift

$$E_0 - E_0^{(0)} \approx \lambda\left(\frac{\hbar}{m\omega}\right)^{n/2}\frac{2^{-n}}{(n/2)!}. \quad (11.44)$$

It is convenient to express this result in terms of the uncertainty $\Delta x = \sqrt{\frac{\hbar}{2m\omega}}$ of position in the ground state, which is the equivalent of the classical oscillation amplitude. One then obtains

$$E_0 - E_0^{(0)} \approx \lambda(\Delta x)^n \frac{2^{-n/2}}{(n/2)!}, \quad (n \text{ even}). \quad (11.45)$$

Note that the numerical coefficient rapidly falls of with increasing $n$.

## XII. QUANTUM MECHANICS IN THREE DIMENSIONS

### A. Coordinates and wavefunction

Three-dimensional space $\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$ is spanned by three basis vectors $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ with coordinates $x$, $y$ and $z$.

The state of a system is described by a wavefunction $\psi(\mathbf{r}) = \psi(x, y, z)$.

### B. Position operators

The coordinates are associated with three position operators $\hat{x}$, $\hat{y}$, $\hat{z}$ which act as

$$\hat{x}\psi(\mathbf{r}) = x\psi(\mathbf{r}), \quad \hat{y}\psi(\mathbf{r}) = y\psi(\mathbf{r}), \quad \hat{z}\psi(\mathbf{r}) = z\psi(\mathbf{r}). \quad (12.1)$$

These coordinates commute since $(\hat{x}\hat{y} - \hat{y}\hat{x})\psi(x, y, z) = xy\psi(x, y, z) - yx\psi(x, y, z) = 0$ etc. Hence $[\hat{x}, \hat{y}] = 0$, $[\hat{x}, \hat{z}] = 0$, $[\hat{y}, \hat{z}] = 0$. Therefore, $x$, $y$ and $z$ are simultaneous observables (they can be measured simultaneously without affecting each other). Indeed, Heisenberg's uncertainty relation gives, e.g., $\Delta x \Delta y \geq 0$, so that it is possible to determine both $x$ and $y$ with no uncertainty, $\Delta x = \Delta y = 0$.

### C. Momentum operators

Momentum $\mathbf{p} = p_x\mathbf{i} + p_y\mathbf{j} + p_z\mathbf{k}$ is associated with momentum operators

$$\hat{p}_x = -i\hbar\frac{\partial}{\partial x}, \quad \hat{p}_y = -i\hbar\frac{\partial}{\partial y}, \quad \hat{p}_z = -i\hbar\frac{\partial}{\partial z}, \quad (12.2)$$

which act as

$$\hat{p}_x\psi(\mathbf{r}) = -i\hbar\frac{\partial\psi(\mathbf{r})}{\partial x}, \quad (12.3)$$

$$\hat{p}_y\psi(\mathbf{r}) = -i\hbar\frac{\partial\psi(\mathbf{r})}{\partial y}, \quad (12.4)$$

$$\hat{p}_z\psi(\mathbf{r}) = -i\hbar\frac{\partial\psi(\mathbf{r})}{\partial z}. \quad (12.5)$$

The momentum operators commute with each other because the order of differentiation does not matter for any function $\psi(\mathbf{r})$:

$$\frac{\partial^2\psi(\mathbf{r})}{\partial x\partial y} = \frac{\partial^2\psi(\mathbf{r})}{\partial y\partial x}. \quad (12.6)$$

Hence $[\hat{p}_x, \hat{p}_y] = 0$, $[\hat{p}_x, \hat{p}_z] = 0$, $[\hat{p}_y, \hat{p}_z] = 0$.

### D. Commutators between position and momentum

From one dimension we already know $[\hat{x}, \hat{p}_x] = i\hbar$. This also translates to the commutators $[\hat{y}, \hat{p}_y] = i\hbar$, $[\hat{z}, \hat{p}_z] = i\hbar$.

However, the following commutators vanish: $[\hat{x}, \hat{p}_y] = 0$, $[\hat{x}, \hat{p}_z] = 0$, $[\hat{y}, \hat{p}_x] = 0$, $[\hat{y}, \hat{p}_z] = 0$, $[\hat{z}, \hat{p}_x] = 0$, $[\hat{z}, \hat{p}_y] = 0$.

### E. Momentum eigenstates

The normalised momentum eigenfunctions in three dimensions are given by

$$\psi_{\mathbf{p}}(\mathbf{r}) = (2\pi\hbar)^{-3/2}\exp(i\mathbf{p}\cdot\mathbf{r}/\hbar) \quad (12.7)$$

where $\mathbf{p} = p_x\mathbf{i} + p_y\mathbf{j} + p_z\mathbf{k}$.

They can also be written as

$$\psi_{\mathbf{p}}(\mathbf{r}) = \psi_{p_x}(x)\psi_{p_y}(y)\psi_{p_z}(z) \quad (12.8)$$

where $\psi_p(x) = (2\pi\hbar)^{-1/2}\exp(ipx/\hbar)$.

Indeed we find

$$\hat{p}_x\psi_{\mathbf{p}}(\mathbf{r}) = p_x\psi_{\mathbf{p}}(\mathbf{r}), \quad (12.9)$$

$$\hat{p}_y\psi_{\mathbf{p}}(\mathbf{r}) = p_y\psi_{\mathbf{p}}(\mathbf{r}), \quad (12.10)$$

$$\hat{p}_z\psi_{\mathbf{p}}(\mathbf{r}) = p_z\psi_{\mathbf{p}}(\mathbf{r}). \quad (12.11)$$

### F. Dirac notation

In Dirac notation, we denote states as $|\psi\rangle$. In order to establish the connection to the wave function $\psi(\mathbf{r})$ in three dimensions, we employ the position basis $|\mathbf{r}\rangle$ with $\hat{x}|\mathbf{r}\rangle = x|\mathbf{r}\rangle$ etc, and write

$$|\psi\rangle = \iiint d\mathbf{r}\,\psi(\mathbf{r})|\mathbf{r}\rangle. \quad (12.12)$$

Alternatively, we may use the momentum basis $|\mathbf{p}\rangle$ with $\hat{p}_x|\mathbf{p}\rangle = p_x|\mathbf{p}\rangle$ etc, and write

$$|\psi\rangle = \iiint d\mathbf{p}\,\tilde{\psi}(\mathbf{p})|\mathbf{p}\rangle. \quad (12.13)$$

As $\langle\mathbf{r}|\mathbf{p}\rangle = (2\pi\hbar)^{-3/2}\exp(i\mathbf{p}\cdot\mathbf{r}/\hbar)$, the expansion coefficients $\psi(\mathbf{r}) = \langle\mathbf{r}|\psi\rangle$ and $\tilde{\psi}(\mathbf{p}) = \langle\mathbf{p}|\psi\rangle$ in both basis sets are related by a three-dimensional Fourier transformation,

$$\psi(\mathbf{r}) = \iiint d\mathbf{p}\,\tilde{\psi}(\mathbf{p})\langle\mathbf{r}|\mathbf{p}\rangle. \quad (12.14)$$

## G. Schrödinger equation in three dimensions

In three dimensions the Hamiltonian for a point particle of mass $m$ is given by

$$\hat{H} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} + V(\hat{\mathbf{r}}) = -\frac{\hbar^2}{2m}\Delta + V(\hat{\mathbf{r}}) \quad (12.15)$$

where $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplace operator. In position representation, the stationary Schrödinger equation $E|\psi\rangle = \hat{H}|\psi\rangle$ is given by

$$E\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}). \quad (12.16)$$

## XIII. THREE-DIMENSIONAL EXAMPLES AND APPLICATIONS

### A. Example: free particle in three dimensions

The Hamiltonian of a free particle is given by

$$\hat{H} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} = -\frac{\hbar^2}{2m}\Delta, \quad (13.1)$$

and the associated Schrödinger equation is

$$E\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r}). \quad (13.2)$$

The solutions are the momentum eigenstates $\psi_{\mathbf{p}}(\mathbf{r})$ given in Eq. (12.7):

$$E\psi_{\mathbf{p}}(\mathbf{r}) = \frac{p^2}{2m}\psi_{\mathbf{p}}(\mathbf{r}) \quad (13.3)$$

where $p^2 = p_x^2 + p_y^2 + p_z^2$.

### B. Separation of variables in cartesian coordinates

In this course we will only consider problems which can be reduced to one-dimensional sub-problems. In the simplest case, this reduction can be carried out in cartesian coordinates: if $V(\mathbf{r}) = V_1(x) + V_2(y) + V_3(z)$ then we can find solutions of the form $\psi(\mathbf{r}) = X(x)Y(y)Z(z)$.

Proof: Insert $\psi(\mathbf{r}) = X(x)Y(y)Z(z)$ into the Schrödinger equation:

$$\begin{aligned}
&EX(x)Y(y)Z(z) \\
&= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}X(x) + V_1(x)X(x)\right)Y(y)Z(z) \\
&+ \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}Y(y) + V_2(y)Y(y)\right)X(x)Z(z) \\
&+ \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}Z(z) + V_3(z)Z(z)\right)X(x)Y(y).(13.4)
\end{aligned}$$

Devide both sides by $X(x)Y(y)Z(z)$:

$$\begin{aligned}
E = &\frac{1}{X(x)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}X(x) + V_1(x)X(x)\right) \\
&+ \frac{1}{Y(y)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}Y(y) + V_2(y)Y(y)\right) \\
&+ \frac{1}{Z(z)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}Z(z) + V_3(z)Z(z)\right).(13.5)
\end{aligned}$$

Since the left hand side of this equation is constant and each of the terms on the right hand side only depends on one of the three variables, each of those terms has to be constant. This gives three one-dimensional Schrödinger equations

$$E_1 X(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X(x) + V_1(x)X(x), \quad (13.6)$$

$$E_2 Y(y) = -\frac{\hbar^2}{2m}\frac{d^2}{dy^2}Y(y) + V_2(y)Y(y), \quad (13.7)$$

$$E_3 Z(z) = -\frac{\hbar^2}{2m}\frac{d^2}{dz^2}Z(z) + V_3(z)Z(z). \quad (13.8)$$

The total energy is $E = E_1 + E_2 + E_3$.

### C. Example: particle in the box

A three-dimensional box is defined by the potential $V(\mathbf{r}) = 0$ for $0 < x < L_1$ and $0 < y < L_2$ and $0 < z < L_3$ while $V(\mathbf{r}) = \infty$ elsewhere.

This potential can be written in the form $V(\mathbf{r}) = V_1(x) + V_2(y) + V_3(z)$ where

$$V_1(x) = 0 \text{ for } 0 < x < L_1, \quad V_1(x) = \infty \text{ elsewhere},$$
$$V_2(y) = 0 \text{ for } 0 < y < L_2, \quad V_2(y) = \infty \text{ elsewhere},$$
$$V_3(z) = 0 \text{ for } 0 < z < L_3, \quad V_3(z) = \infty \text{ elsewhere}.$$

The three equations (13.6,13.7,13.8) are of the form of one-dimensional particles in the box and are solved by

$$X(x) = \sqrt{\frac{2}{L_1}}\sin\frac{n_1\pi x}{L_1}, \quad E_1 = \frac{n_1^2\pi^2\hbar^2}{2mL_1^2} \quad (13.9)$$

$$Y(y) = \sqrt{\frac{2}{L_2}}\sin\frac{n_2\pi y}{L_2}, \quad E_2 = \frac{n_2^2\pi^2\hbar^2}{2mL_2^2} \quad (13.10)$$

$$Z(z) = \sqrt{\frac{2}{L_3}}\sin\frac{n_3\pi z}{L_3}, \quad E_3 = \frac{n_3^2\pi^2\hbar^2}{2mL_3^2} \quad (13.11)$$

The total energy is

$$E = E_1 + E_2 + E_3 = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right). \quad (13.12)$$

The numbers $n_1 = 1, 2, 3, \ldots$, $n_2 = 1, 2, 3, \ldots$, $n_3 = 1, 2, 3, \ldots$ which enumerate the energies are also called *quantum numbers*.

## D. Degeneracy

For a symmetric box with $L_1 = L_2 = L_3 = L$ the energies are

$$E = \frac{\pi^2 \hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2).  \quad (13.13)$$

It is then possible to have *degeneracy*: Different sets of quantum numbers $(n_1, n_2, n_3)$ (hence, different eigenfunctions) can have the same energy. The degeneracy factor is generally denoted as $g$. For example: the six combinations $(n_1, n_2, n_3) = (1, 2, 3)$, $(2, 3, 1)$, $(3, 1, 2)$, $(1, 3, 2)$, $(2, 1, 3)$, $(3, 2, 1)$ all give the same energy $E = 14\frac{\pi^2 \hbar^2}{2mL^2}$. This is then called a six-fold degenerate energy level ($g = 6$).

## E. Density of states

For many physical problems (such as thermodynamics, or transitions in scattering or decay processes, to be encountered later in this course), we need to know the number of states with energies $E_n \approx E$, without resolving the details of the energy quantisation. This number can be estimated by first considering the number of states with energy $E_n < E$,

$$N(E) = \sum_n \Theta(E - E_n)  \quad (13.14)$$

[where $\Theta(x)$ is the *unit step function*, with $\Theta(x) = 0$ for $x < 0$ and $\Theta(x) = 1$ for $x > 1$], and then smoothing this out over energy to obtain a continuous function $\bar{N}(E)$ to finally obtain the *density of states*

$$\rho(E) = d\bar{N}/dE.  \quad (13.15)$$

This quantity is large in regions where levels are closely spaced [the level spacing is $\Delta E = 1/\rho(E)$].

For the particle in the three-dimensional box, we can carry out this program by replacing the sum over the quantum numbers by an integral over a continuous three-dimensional vector $\mathbf{n} = (n_1, n_2, n_3)$ (with all components positive), and interpreting $E = \pi^2 \hbar^2 |\mathbf{n}|^2 / 2mL^2$ as a continuous function of this vector. In the space of $\mathbf{n}$, the allowed states populate a volume

$$N(E) = \frac{1}{8}\frac{4\pi}{3}|\mathbf{n}|^3 = \frac{(2m)^{3/2}L^3}{6\pi^2 \hbar^3}E^{3/2},  \quad (13.16)$$

and the density of states becomes

$$\rho(E) = \frac{(2m)^{3/2}L^3}{4\pi^2 \hbar^3}E^{1/2}.  \quad (13.17)$$

Since this expression is proportional to the volume of the box, it is advantageous to introduce the *local density of states*

$$\nu(E) = \rho(E)/L^3 = \frac{(2m)^{3/2}}{4\pi^2 \hbar^3}E^{1/2}.  \quad (13.18)$$

Analogously, in two dimensions one obtains

$$\nu(E) = \frac{m}{2\pi \hbar^2}  \quad (13.19)$$

(i.e., a constant), while in one dimension

$$\nu(E) = \frac{1}{2\pi \hbar}\sqrt{\frac{2m}{E}}.  \quad (13.20)$$

To a very good approximation, these expressions also apply to charge carriers in metals or semiconductors, if one only replaces the mass $m$ by a suitable *effective mass* $m^*$ which accounts for the forces from the ionic background in the material. E.g., in GaAs, $m^* \approx 0.067 m_e$ for electron-like carriers, where $m_e$ the electron mass. Such materials allow to realize particle boxes of various dimensions (quantum wells, nanowires, and quantum dots) by suitable position-dependent doping and gating. Furthermore, since electrons carry an additional degree of freedom called spin (which we discuss in section XVI), the density of state has to be multiplied by a factor of two.

For massless particles like photons, the density of states can be constructed analogously by using the dispersion relation $E = \hbar\omega = \hbar ck$. In three dimensions, accounting for the two polarisation directions of the photon we then obtain the local density of states

$$\nu(E) = \frac{E^2}{\pi^2 \hbar^3 c^3}  \quad (13.21)$$

(as we will discuss later, each of these states can carry multiple photons). A related example is graphene, a two-dimensional sheet of carbon atoms, where electrons have dispersion relation $E = \hbar v_F |\mathbf{k}|$ with constant Fermi velocity $v_F \sim 10^6 m/s$. Accounting for all internal degrees of freedom (spin and *pseudospin*), the local density of states in this material is $\nu(E) = 2|E|/(\pi \hbar^2 v_F^2)$.

## F. Example: harmonic oscillator

### 1. Revision of the one-dimensional harmonic oscillator

In one dimension, the Schrödinger equation

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi(x),  \quad (13.22)$$

of the harmonic oscillator is solved by

$$E_n = \hbar\omega(n + 1/2), \qquad (13.23)$$

$$\psi_n(x) = \sqrt{\frac{\alpha}{\pi^{1/2}2^n n!}} H_n(\alpha x)e^{-\alpha^2 x^2/2} \qquad (13.24)$$

where $\alpha = \sqrt{\frac{m\omega}{\hbar}}$ and the first Hermite polynomials are $H_0(s) = 1$, $H_1(s) = 2s$, $H_2(s) = 4s^2 - 2$.

## 2. The three-dimensional harmonic oscillator

The three-dimensional oscillator has potential energy

$$V(\mathbf{r}) = V_1(x) + V_2(y) + V_3(z), \qquad (13.25)$$

$$V_1(x) = \frac{1}{2}m\omega_1^2 x^2, \qquad (13.26)$$

$$V_2(y) = \frac{1}{2}m\omega_2^2 y^2, \qquad (13.27)$$

$$V_3(z) = \frac{1}{2}m\omega_3^2 z^2. \qquad (13.28)$$

Hence the three equations (13.6,13.7,13.8) are of the form of three one-dimensional harmonic oscillators

$$E_1 X(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}X(x) + \frac{1}{2}m\omega_1^2 x^2 X(x), \quad (13.29)$$

$$E_2 Y(y) = -\frac{\hbar^2}{2m}\frac{d^2}{dy^2}Y(y) + \frac{1}{2}m\omega_2^2 y^2 Y(y), \quad (13.30)$$

$$E_3 Z(z) = -\frac{\hbar^2}{2m}\frac{d^2}{dz^2}Z(z) + \frac{1}{2}m\omega_3^2 z^2 Z(z). \quad (13.31)$$

and are solved by

$$X(x) = \sqrt{\frac{\alpha_1}{\pi^{1/2}2^{n_1} n_1!}} H_{n_1}(\alpha_1 x)e^{-\alpha_1^2 x^2/2}, \quad (13.32)$$

$$Y(y) = \sqrt{\frac{\alpha_2}{\pi^{1/2}2^{n_2} n_2!}} H_{n_2}(\alpha_2 y)e^{-\alpha_2^2 y^2/2}, \quad (13.33)$$

$$Z(z) = \sqrt{\frac{\alpha_3}{\pi^{1/2}2^{n_3} n_3!}} H_{n_3}(\alpha_3 z)e^{-\alpha_3^2 z^2/2}. \quad (13.34)$$

where $\alpha_i = \sqrt{\frac{m\omega_i}{\hbar}}$. The individual energies are $E_i = \hbar\omega_i(n_i + 1/2)$ and the total energy is

$$E = \hbar\omega_1\left(n_1+\frac{1}{2}\right)+\hbar\omega_2\left(n_2+\frac{1}{2}\right)+\hbar\omega_3\left(n_3+\frac{1}{2}\right), \quad n_i = 0, 1, 2, \ldots$$
$$(13.35)$$

## 3. Degeneracy and density of states of the isotropic oscillator

When all three frequencies $\omega_1 = \omega_2 = \omega_3 = \omega$ are identical then the potential $V(\mathbf{r}) = \frac{1}{2}m\omega^2|\mathbf{r}|^2$ depends only on the radial distance from the origin,

hence it is spherical symmetric. This is called the isotropic harmonic oscillator (isotropic means independent of the direction). The energy levels are now given by $E = \hbar\omega(n_1 + n_2 + n_3 + 3/2)$. Hence, different states with the same sum of quantum numbers $n_1 + n_2 + n_3$ have the same energy. Therefore, each level with energy $E_n = \hbar\omega(n + 3/2)$ has degeneracy $g_n = (n + 1)(n + 2)/2$. It follows that the (smoothed) number of states with energy less than $E$ is given by $\bar{N}(E) = E^3/6(\hbar\omega)^3$, and the density of states is $\rho(E) = E^2/2(\hbar\omega)^3$. (In two dimensions, $\rho(E) = E/\hbar^2\omega^2$, and in one dimension $\rho(E) = 1/\hbar\omega$, where the latter is a constant in accordance with the constant level spacing $\Delta E = \hbar\omega$.)

## XIV. CENTRAL POTENTIALS

The isotropic harmonic oscillator is an example of a spherical symmetric potential, where the potential energy only depends on the radial distance from the origin, $r = |\mathbf{r}|$. These potentials are called central potentials. Another example is the Coulomb potential

$$V_c = \frac{q_1 q_2}{4\pi\varepsilon_0 r} \qquad (14.1)$$

of two charges $q_1$ and $q_2$. For central potentials the Schrödinger equation

$$E\psi(\mathbf{r}) = -\frac{\hbar^2}{2\mu}\Delta\psi(\mathbf{r}) + V(r)\psi(\mathbf{r}) \qquad (14.2)$$

can also be separated in three one-dimensional problems, but only when one works in spherical polar coordinates. Note: Here mass is denoted by the symbol $\mu$ since we need $m$ later for a different purpose.

### A. Spherical polar coordinates

The three spherical coordinates are the radial coordinate $r = \sqrt{x^2 + y^2 + z^2}$, the azimuthal angle $\phi = \arctan(y/x)$, and the polar angle $\theta = \arccos(z/r)$. The cartesian coordinates can be written as

$$x = r\sin\theta\cos\phi, \qquad (14.3)$$
$$y = r\sin\theta\sin\phi, \qquad (14.4)$$
$$z = r\cos\theta. \qquad (14.5)$$

The Laplace operator is given by

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}.$$
$$(14.6)$$

We abbreviate the angular part as

$$\Delta_{\theta,\phi} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}. \qquad (14.7)$$
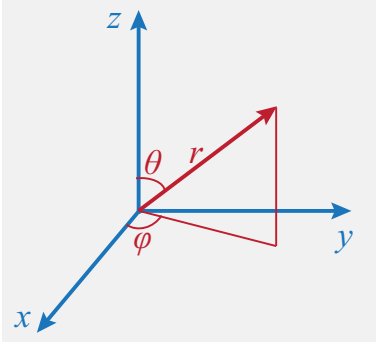
FIG. 1 Spherical polar coordinates.

## B. Separation of variables in spherical polar coordinates

We separate the radial dependence from the angular dependence in the wavefunction, $\psi(x, y, z) = R(r)Y(\theta, \phi)$. From the Schrödinger equation (14.2) one finds that the angular part solves the equation $\Delta_{\theta,\phi}Y = -l(l+1)Y$, i.e.,

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = -l(l+1)Y, \quad (14.8)$$

while the radial part solves the equation

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right)R = ER, \quad (14.9)$$

where $l$ is a constant.

## C. Angular part

Since Eq. (14.8) for the angular part does not depend on the potential $V(r)$ we can solve this equation once and for all. The solutions are the *spherical harmonics*

$$Y_{lm}(\theta, \phi) = (-1)^m\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\phi}, \quad (14.10)$$

for $m \geq 0$, $Y_{l,-m}(\theta, \phi) = (-1)^m Y_{l,m}^*(\theta, \phi)$ for $m < 0$.

Here $l = 0, 1, 2, 3, \ldots$ is called the *azimuthal quantum number* and $m = 0, \pm 1, \pm 2, \ldots, \pm l$ is called the *magnetic quantum number*. Note that for each $l$ there are $2l+1$ values of $m$.

For $m = 0$ the functions $P_l^m(s)$ are the Legendre polynomials

$$P_l^0(s) = \frac{1}{2^l l!}\frac{d^l}{ds^l}(s^2 - 1)^l, \quad l = 0, 1, 2, 3, \ldots. \quad (14.11)$$

Hence

$$P_0^0(s) = 1, \quad (14.12)$$
$$P_1^0(s) = s, \quad (14.13)$$
$$P_2^0(s) = (3s^2 - 1)/2, \quad (14.14)$$
$$P_3^0(s) = (5s^3 - 3s)/2. \quad (14.15)$$

For $m \neq 0$ the functions $P_l^m(s)$ are the associated Legendre polynomials

$$P_l^m(s) = P_l^{-m}(s) = (1 - s^2)^{|m|/2}\frac{d^{|m|}}{ds^{|m|}}P_l^0(s). \quad (14.16)$$

The first spherical harmonics are

$$Y_{00}(\theta, \phi) = \sqrt{\frac{1}{4\pi}} \quad \text{for } l = 0, \, m = 0, \quad (14.17)$$

$$Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}}\cos\theta \quad \text{for } l = 1, \, m = 0, \quad (14.18)$$

$$Y_{1,\pm 1}(\theta, \phi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi} \quad \text{for } l = 1, \, m = \pm 1, \quad (14.19)$$

$$Y_{20}(\theta, \phi) = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1), \quad (14.20)$$

$$Y_{2,\pm 1}(\theta, \phi) = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}, \quad (14.21)$$

$$Y_{2,\pm 2}(\theta, \phi) = \mp\sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\phi}, \quad (14.22)$$

## D. Quantisation of angular momentum

The angular momentum operator is given by $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$, hence $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$ etc. The squared length is given by $\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. One can show that

$$\hat{\mathbf{L}}^2 Y_{lm}(\theta, \phi) = \hbar^2 l(l+1)Y_{lm}, \quad (14.23)$$

$$\hat{L}_z Y_{lm}(\theta, \phi) = \hbar m Y_{lm}. \quad (14.24)$$

Hence the spherical harmonics are eigenfunctions of $\hat{\mathbf{L}}^2$ and $\hat{L}_z$, with eigenvalues $\hbar^2 l(l+1)$ and $\hbar m$, respectively.

## E. Degeneracy of the radial part

Equation (14.9) for the radial part $R(r)$ depends on the potential and hence has to be solved separately for every problem in order to find the energies $E$. However, since this equation only depends on the azimuthal quantum number $l$ but not on the magnetic quantum number $m$, each energy level is at least $2l+1$ fold degenerate, since for each $l$ there are $2l+1$ solutions $Y_{lm}$ of the angular equation with different values of $m$.

## XV. ANGULAR MOMENTUM

### A. Classical angular momentum and magnetic moment

Classical angular momentum is given by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = (yp_z - zp_y)\mathbf{i} + (zp_x - xp_z)\mathbf{j} + (xp_y - yp_x)\mathbf{k}. \tag{15.1}$$



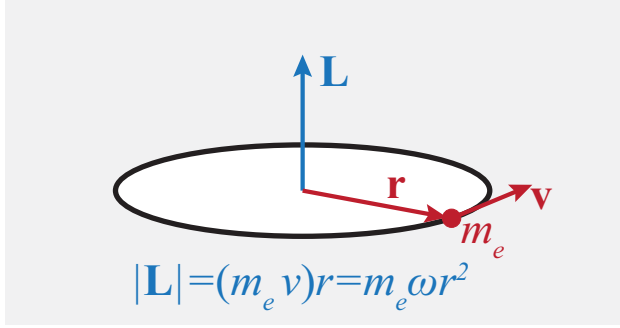$$|\mathbf{L}| = (m_e v)r = m_e \omega r^2$$

FIG. 2 Illustration of classical angular momentum.

### B. Angular momentum operators

The angular momentum operator $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$ has components

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \tag{15.2}$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \tag{15.3}$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \tag{15.4}$$

Total angular momentum is given by

$$\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\Delta_{\theta,\phi}. \tag{15.5}$$

The commutation relations are

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \quad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x, \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y, \tag{15.6}$$

$$[\hat{L}_x, \hat{\mathbf{L}}^2] = 0, \quad [\hat{L}_y, \hat{\mathbf{L}}^2] = 0, \quad [\hat{L}_z, \hat{\mathbf{L}}^2] = 0. \tag{15.7}$$

Heisenberg's uncertainty principle dictates that it is not possible to know two components of angular momentum at the same time (since their commutator does not vanish). However, it is possible to determine one of the components (say $L_z$) simultaneously with the total angular momentum, since $[\hat{L}_z, \hat{\mathbf{L}}^2] = 0$.

### C. Angular momentum eigenfunctions

We already determined that the spherical harmonics $Y_{lm}$ are joint eigenfunctions of $\hat{\mathbf{L}}^2$ and $\hat{L}_z$,

$$\hat{\mathbf{L}}^2 Y_{lm}(\theta, \phi) = \hbar^2 l(l+1)Y_{lm}, \tag{15.8}$$

$$\hat{L}_z Y_{lm}(\theta, \phi) = \hbar m Y_{lm}. \tag{15.9}$$

The eigenvalues are $\hbar^2 l(l+1)$ and $\hbar m$, respectively. E.g., for $l = 2$ the length of the angular momentum vector is $|\mathbf{L}| = \sqrt{6}\hbar$ and there are 5 possible values values of $L_z$, as is illustrated in the following figure.
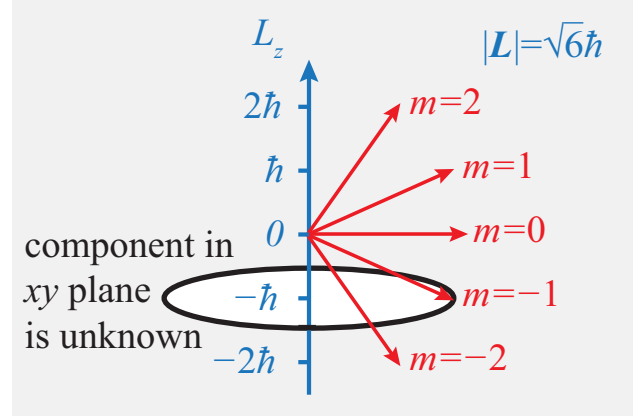


FIG. 3 Angular momentum quantisation.

### D. Angular momentum in Dirac notation

Instead of interpreting the angular Schrödinger equation as a differential equation, this equation can be solved very efficiently by employing the perspective of operators and vectors.

In Dirac notation, the eigenstates of the $\hat{L}_z$ and $\hat{\mathbf{L}}^2$ are denoted as $|lm\rangle$, such that

$$\hat{L}_z|lm\rangle = \hbar m|lm\rangle, \quad \hat{\mathbf{L}}^2|lm\rangle = \hbar^2 l(l+1)|lm\rangle. \tag{15.10}$$

We now introduce the *ladder operators* $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$, which are *non-hermitian* and related by $\hat{L}_+^\dagger = \hat{L}_-$. These operators fulfill the commutation relation

$$[\hat{L}_z, \hat{L}_\pm] = [\hat{L}_z, \hat{L}_x] \pm i[\hat{L}_z, \hat{L}_y] = i\hbar\hat{L}_y \pm \hbar L_x = \pm\hbar L_\pm. \tag{15.11}$$

The utility of these operators arises from the fact that they relate the eigenstates $|lm\rangle$ of fixed $l$ but different $m$ in a systematic way. Indeed, the following calculation shows that $\hat{L}_\pm|lm\rangle$ is still an eigenstate of $L_z$,

$$\hat{L}_z(\hat{L}_\pm|lm\rangle) = \hat{L}_\pm\hat{L}_z|lm\rangle + [\hat{L}_z, \hat{L}_\pm]|lm\rangle = \hbar(m\pm1)\hat{L}_\pm|lm\rangle, \tag{15.12}$$

with eigenvalue $\hbar(m \pm 1)$. Furthermore, because $[\hat{\mathbf{L}}^2, \hat{L}_\pm] = 0$ this state is also an eigenstate of $\hat{\mathbf{L}}^2$, with eigenvalue $\hbar^2 l(l+1)$. Thus,

$$\hat{L}_\pm |l, m\rangle = c_{lm}^\pm |l, m \pm 1\rangle, \qquad (15.13)$$

where the normalisation constants work out as

$$c_{lm}^+ = \hbar\sqrt{(l-m)(l+m+1)}, \quad c_{lm}^- = c_{l,-m}^+. \quad (15.14)$$

Since $c_{ll}^+ = 0$, the state $|ll\rangle$ is determined by the condition

$$\hat{L}_+ |ll\rangle = |0\rangle, \qquad (15.15)$$

while all other states follow by repeated application of $\hat{L}_-$.

This construction of the angular momentum eigenstates and determination of their eigenvalues is purely algebraic, and sidesteps any explicit reference to spherical harmonics. Their explicit form can be recovered by writing $\langle \theta, \phi | lm \rangle = Y_{lm}(\theta, \phi)$, where $|\theta, \phi\rangle$ denotes position basis states on the unit sphere, parameterised in spherical polar coordinates. $Y_{ll}$ is then obtained from Eq. (15.15), where $\hat{L}_+$ is expressed as the associated differential operator, and the other spherical harmonics follow by successive application of the differential operator associated with $\hat{L}_-$.

### E. Magnetic moment

The orbital motion of an electron with angular momentum $\mathbf{L}$ gives rise to a magnetic moment

$$\mathbf{m} = -\frac{e}{2m_e}\mathbf{L}. \qquad (15.16)$$

When a magnetic field $\mathbf{B}$ is applied, this gives rise to an interaction energy

$$V_B = -\mathbf{m} \cdot \mathbf{B}, \qquad (15.17)$$

which can be used to measure the angular momentum. We assume that the magnetic field is applied in $z$ direction, $\mathbf{B} = B_z\mathbf{k}$, therefore

$$V_B = \frac{eB_z}{2m_e}L_z. \qquad (15.18)$$

Quantum mechanically the interaction energy is represented by the operator

$$\hat{V}_B = \frac{eB_z}{2m_e}\hat{L}_z. \qquad (15.19)$$

In a central potential a magnetic field hence lifts the $2l+1$ fold degeneracy of the angular part of the
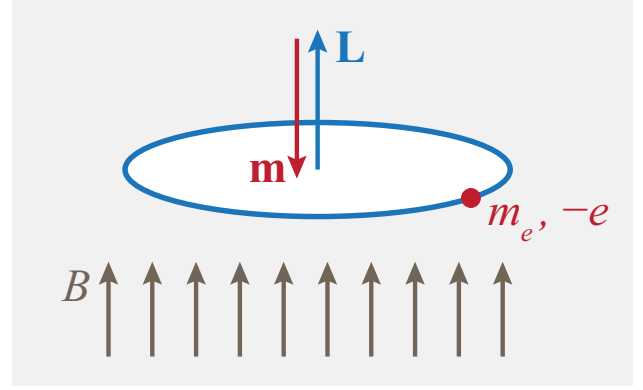


FIG. 4 Magnetic moment.

wavefunction: For each value of m, the energies of the orbitals are shifted by an amount

$$\delta E_m = \mu_B B_z m, \qquad (15.20)$$

which depends on the magnetic quantum number $m$ (hence the name). Here $\mu_B = \frac{e\hbar}{2m_e}$ is the so-called Bohr magneton.

### XVI. SPIN

The electron also has an intrinsic angular momentum $\hat{\mathbf{S}}$, independently of its orbital angular momentum $\hat{\mathbf{L}}$. This intrinsic angular momentum is called spin (the name suggests that the electron performs a rotation around itself, which is, however, actually not the case).
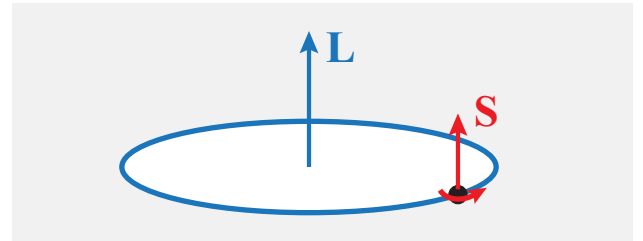


FIG. 5 Spin.

### A. Stern-Gerlach experiment

The spin was discovered in the Stern-Gerlach experiment in 1922. In this experiment, silver atoms are heated in an oven, from which they escape through a tiny hole. They travel into $x$ direction and enter an apparatus where they pass through an inhomogeneous magnetic field $\mathbf{B} = bz\mathbf{k}$. This field points into $z$ direction and has a finite gradient $\partial B_z/\partial z = b$. If the atoms carry a magnetic
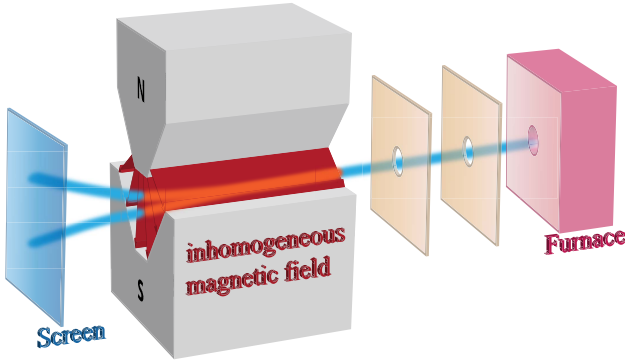
FIG. 6 Set-up of the Stern-Gerlach experiment.

moment **m** this gives rise to a force

$$F_z = -\frac{\partial V_B}{\partial z} = m_z b \qquad (16.1)$$

which deflects the atoms into $z$ direction. In the experiment it is observed that the atoms arrive on the screen at two spots, only. This is not what is classically expected, but also incompatible with quantisation of the orbital angular momentum **L**, which always yields an odd number $2l+1$ of possible values of $F_z$ since $l$ is an integer. However, the experiment can be fully explained by introducing an intrinsic magnetic moment

$$\hat{\mathbf{m}} = -\frac{e}{m_e}\hat{\mathbf{S}}, \qquad (16.2)$$

where $\hat{\mathbf{S}}$ has the properties of angular momentum, but with $l = l_s = 1/2$ not an integer. Since the spin magnetic quantum number is restricted to $m_s = -l_s, -l_s + 1, \ldots, l_s$ this allows only two values $m_s = \pm\frac{1}{2}$, hence

$$S_z = \frac{\hbar}{2} \text{ or } S_z = -\frac{\hbar}{2}. \qquad (16.3)$$

Given the force from Eq. (16.1) it can be deduced that the observed locations of the arriving atoms indeed correspond to these two values.

### B. Spinor

The spin state of the electron is described by a two-component vector (called spinor)

$$\psi = \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix} \qquad (16.4)$$

where

$$|\psi_\uparrow|^2 = \text{probability that } S_z = \hbar/2 \text{ ('spin up'), } (16.5)$$
$$|\psi_\downarrow|^2 = \text{probability that } S_z = -\hbar/2 \text{ ('spin down'). } (16.6)$$

Hence $\psi = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ describes an electron with spin up and $\psi = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ describes an electron with spin down.

The scalar product of spinors is given by (see the mathematical appendix)

$$\langle \psi | \varphi \rangle = \psi_\uparrow^* \varphi_\uparrow + \psi_\downarrow^* \varphi_\downarrow. \qquad (16.7)$$

Normalisation of the probability requires $|\psi_\uparrow|^2 + |\psi_\downarrow|^2 = 1$, hence $\langle \psi | \psi \rangle = 1$.

### C. Spin operators

The spin operator $\hat{\mathbf{S}} = \hat{S}_x\mathbf{i} + \hat{S}_y\mathbf{j} + \hat{S}_z\mathbf{k}$ consists of the three spin matrices

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad (16.8)$$

$$\hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad (16.9)$$

$$\hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \qquad (16.10)$$

The three matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad (16.11)$$

are called *Pauli matrices*.

Matrix multiplication (see the mathematical appendix) gives

$$\hat{\mathbf{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \qquad (16.12)$$

The commutation relations also follow from matrix multiplication,

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z, \quad [\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x, \quad [\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y, \qquad (16.13)$$

$$[\hat{S}_x, \hat{\mathbf{S}}^2] = 0, \quad [\hat{S}_y, \hat{\mathbf{S}}^2] = 0, \quad [\hat{S}_z, \hat{\mathbf{S}}^2] = 0. \qquad (16.14)$$

This is identical to the commutation relations of angular momentum, see Eqs. (15.6) and (15.7).

### D. Eigenvalues and eigenvectors of $\hat{\mathbf{S}}^2$ and $\hat{S}_z$

Since

$$\hat{\mathbf{S}}^2\begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix} = \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix} = \frac{3}{4}\hbar^2\begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix}, \quad (16.15)$$

all vectors are eigenvectors $\hat{\mathbf{S}}^2$. The eigenvalue $\frac{3}{4}\hbar^2$ corresponds to angular momentum with $l = l_s = 1/2$, see Eq. (15.8).

Since

$$\hat{S}_z\begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} \psi_\uparrow \\ -\psi_\downarrow \end{pmatrix}, \quad (16.16)$$

the normalised eigenvectors of $\hat{S}_z$ are $\psi = \binom{1}{0}$ (with eigenvalue $\hbar/2$) and $\psi = \binom{0}{1}$ (with eigenvalue $-\hbar/2$). This again corresponds to angular momentum with $l = l_s = 1/2$, see Eq. (15.9).
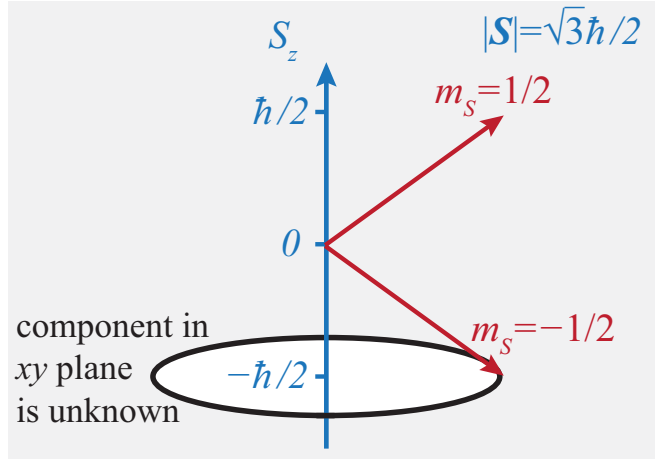


FIG. 7 Quantisation of spin.

### E. Eigenvalues and eigenvectors of $\hat{S}_x$ and $\hat{S}_y$

$$\hat{S}_x \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \psi_\downarrow \\ \psi_\uparrow \end{pmatrix}. \qquad (16.17)$$

Hence the normalised eigenvectors of $\hat{S}_x$ are $\psi = \frac{1}{\sqrt{2}} \binom{1}{1}$ (with eigenvalue $\hbar/2$) and $\psi = \frac{1}{\sqrt{2}} \binom{1}{-1}$ (with eigenvalue $-\hbar/2$).

$$\hat{S}_y \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} -i\psi_\downarrow \\ i\psi_\uparrow \end{pmatrix}. \qquad (16.18)$$

Hence the normalised eigenvectors of $\hat{S}_y$ are $\psi = \frac{1}{\sqrt{2}} \binom{1}{i}$ (with eigenvalue $\hbar/2$) and $\psi = \frac{1}{\sqrt{2}} \binom{1}{-i}$ (with eigenvalue $-\hbar/2$).

### F. Expectation values

The expectation value of $S_z$ is given by

$$
\begin{aligned}
\langle \hat{S}_z \rangle &= \langle \psi | \hat{S}_z \psi \rangle \\
&= \frac{\hbar}{2} (\psi_\uparrow^*, \psi_\downarrow^*) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix} \\
&= \frac{\hbar}{2} (\psi_\uparrow^*, \psi_\downarrow^*) \begin{pmatrix} \psi_\uparrow \\ -\psi_\downarrow \end{pmatrix} \\
&= \frac{\hbar}{2} (|\psi_\uparrow|^2 - |\psi_\downarrow|^2), \qquad (16.19)
\end{aligned}
$$

Note that

$$P(S_z = \hbar/2) = |\psi_\uparrow|^2, \qquad (16.20)$$
$$P(S_z = -\hbar/2) = |\psi_\downarrow|^2. \qquad (16.21)$$

are the probabilities for spin up and down, respectively.

By similar calculations,

$$\langle \hat{S}_x \rangle = \hbar \operatorname{Re} \psi_\uparrow^* \psi_\downarrow, \qquad (16.22)$$
$$\langle \hat{S}_y \rangle = \hbar \operatorname{Im} \psi_\uparrow^* \psi_\downarrow, \qquad (16.23)$$

where Re denotes the real part and Im denotes the imaginary part of the complex number $\psi_\uparrow^* \psi_\downarrow$.

The probabilities for spin measurements in $x$ or $y$ directions are given by

$$P(S_x = \hbar/2) = \frac{1}{2} |\psi_\uparrow + \psi_\downarrow|^2, \qquad (16.24)$$

$$P(S_x = -\hbar/2) = \frac{1}{2} |\psi_\uparrow - \psi_\downarrow|^2, \qquad (16.25)$$

and

$$P(S_y = \hbar/2) = \frac{1}{2} |\psi_\uparrow - i\psi_\downarrow|^2, \qquad (16.26)$$

$$P(S_y = -\hbar/2) = \frac{1}{2} |\psi_\downarrow - i\psi_\uparrow|^2, \qquad (16.27)$$

respectively.

### G. Polarisation vector and Bloch sphere

A convenient alternative way to represent a spinor state is given by the 3-dimensional real *polarisation vector*

$$
\begin{aligned}
\vec{P} &= (\langle \sigma_x \rangle, \langle \sigma_y \rangle, \langle \sigma_z \rangle) \qquad (16.28) \\
&= (2 \operatorname{Re} \psi_\uparrow^* \psi_\downarrow, 2 \operatorname{Im} \psi_\uparrow^* \psi_\downarrow, |\psi_\uparrow|^2 - |\psi_\downarrow|^2). (16.29)
\end{aligned}
$$

If $\psi$ is normalised then the polarisation vector is of unit length, i.e., it is restricted to the surface of a sphere, the so-called *Bloch sphere*.

### H. Stationary Schrödinger equation

The most general stationary Hamiltonian for a spin is a hermitian $2 \times 2$-dimensional matrix. Such a matrix can always be written as

$$H = a_0 I + a_x \sigma_x + a_y \sigma_y + a_z \sigma_z \qquad (16.30)$$

where $a_0$, $a_x$, $a_y$, and $a_z$ are real constants, and

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad (16.31)$$

is the $2 \times 2$-dimensional identity matrix. The stationary Schrödinger equation $E\psi = H\psi$ is solved

by the eigenvectors of $H$. These can be found by writing the vector $\mathbf{a} = (a_x, a_y, a_z) = a\mathbf{n}$, where $\mathbf{n}$ is a unit vector and $a = |\mathbf{a}|$. The eigenvectors can then be written as

$$\psi_+ = \frac{1}{\sqrt{2(1+n_z)}} \begin{pmatrix} 1 + n_z \\ n_x + in_y \end{pmatrix}, \qquad (16.32)$$

$$\psi_- = \frac{1}{\sqrt{2(1+n_z)}} \begin{pmatrix} -n_x + in_y \\ 1 + n_z \end{pmatrix}. \qquad (16.33)$$

On the Bloch sphere, these eigenvectors correspond to the polarisation vectors

$$\vec{P}_\pm = \pm\mathbf{n}. \qquad (16.34)$$

The corresponding eigenvalues

$$E_\pm = a_0 \pm a \qquad (16.35)$$

determine the energy of these states.

### I. Spin in Dirac notation

In order to describe spin in the Dirac notation, we introduce the normalised and mutually orthogonal states $|\uparrow\rangle$ for "spin up" and $|\downarrow\rangle$ for "spin down", with

$$\hat{S}_z|\uparrow\rangle = \frac{\hbar}{2}|\uparrow\rangle, \quad \hat{S}_z|\downarrow\rangle = -\frac{\hbar}{2}|\downarrow\rangle. \qquad (16.36)$$

Accordingly, we can write

$$\hat{S}_z = \frac{\hbar}{2}|\uparrow\rangle\langle\uparrow| - \frac{\hbar}{2}|\downarrow\rangle\langle\downarrow|. \qquad (16.37)$$

The other spin components are then given by the operators

$$\hat{S}_x = \frac{\hbar}{2}|\uparrow\rangle\langle\downarrow| + \frac{\hbar}{2}|\downarrow\rangle\langle\uparrow|, \quad \hat{S}_y = -i\frac{\hbar}{2}|\uparrow\rangle\langle\downarrow| + i\frac{\hbar}{2}|\downarrow\rangle\langle\uparrow|, \qquad (16.38)$$

and the total spin is given as

$$\mathbf{\hat{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{3\hbar^2}{4}(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|). \qquad (16.39)$$

The eigenstates of $\hat{S}_x$ are $|\pm x\rangle = \sqrt{1/2}(|\uparrow\rangle \pm |\downarrow\rangle)$, while those of $\hat{S}_y$ are $|\pm y\rangle = \sqrt{1/2}(|\uparrow\rangle \pm i|\downarrow\rangle)$; the associated eigenvalues are $\pm\hbar/2$. All the expressions for expectation values and probabilities given above can now be seen as special incarnations of our general rules for quantum mechanics, evaluated in the basis $|\uparrow\rangle$, $|\downarrow\rangle$.

In analogy to orbital angular momentum, we can also introduce the ladder operators

$$\hat{S}_+ = \hat{S}_x + iS_y = |\uparrow\rangle\langle\downarrow|, \quad \hat{S}_- = \hat{S}_x - iS_y = |\downarrow\rangle\langle\uparrow|, \qquad (16.40)$$

which are again non-hermitian and related by $\hat{S}_+^\dagger = \hat{S}_-$. These now convert or annihilate spin eigenstates, according to

$$\hat{S}_+|\downarrow\rangle = |\uparrow\rangle, \quad \hat{S}_+|\uparrow\rangle = |0\rangle, \quad \hat{S}_-|\uparrow\rangle = |\downarrow\rangle, \quad \hat{S}_-|\downarrow\rangle = |0\rangle. \qquad (16.41)$$

### J. Mathematical appendix: two-dimensional linear algebra

#### 1. Vectors and matrices

A vector $\mathbf{v}$ in two dimensions is given by two numbers $v_1$ and $v_2$, called components,

$$\mathbf{v} = \begin{pmatrix} v_1 \\ v_2 \end{pmatrix}. \qquad (16.42)$$

Matrices $A$, $B$ etc are given by four numbers, such as

$$A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}, \qquad (16.43)$$

$$B = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix}. \qquad (16.44)$$

We consider the case that the matrix and vector components can be complex numbers.

#### 2. Addition of vectors and matrices

Vectors and matrices are added element by element,

$$\mathbf{v} + \mathbf{w} = \begin{pmatrix} v_1 + w_1 \\ v_2 + w_2 \end{pmatrix}, \qquad (16.45)$$

$$A + B = \begin{pmatrix} a_{11} + b_{11} & a_{12} + b_{12} \\ a_{21} + b_{21} & a_{22} + b_{22} \end{pmatrix}. \qquad (16.46)$$

#### 3. Scalar product

The scalar product

$$\langle\mathbf{v}|\mathbf{w}\rangle = v_1^* w_1 + v_2^* w_2 \qquad (16.47)$$

can also be written as the product

$$\langle\mathbf{v}|\mathbf{w}\rangle = \mathbf{v}^\dagger \mathbf{w}, \qquad (16.48)$$

where $\mathbf{v}^\dagger = (v_1^*, v_2^*)$ denotes the hermitian conjugate.

A vector is said to be normalised when $\langle\mathbf{v}|\mathbf{v}\rangle = 1$.

## 4. Multiplication of a vector and a matrix

When a vector $\mathbf{v}$ is multiplied by a matrix $A$, the result is a new vector $A\mathbf{v}$ with components

$$A\mathbf{v} = \begin{pmatrix} a_{11}v_1 + a_{12}v_2 \\ a_{21}v_1 + a_{22}v_2 \end{pmatrix}. \qquad (16.49)$$

One can also multiply two matrices $A$ and $B$, which results in another matrix

$$AB = \begin{pmatrix} a_{11}b_{11} + a_{12}b_{21} & a_{11}b_{12} + a_{12}b_{22} \\ a_{21}b_{11} + a_{22}b_{21} & a_{21}b_{12} + a_{22}b_{22} \end{pmatrix}. \qquad (16.50)$$

Note that this is different from element-by-element multiplication.

## 5. Eigenvalues and eigenvectors

Given is a matrix $A$. The eigenvalue equation

$$A\mathbf{v} = \lambda\mathbf{v} \qquad (16.51)$$

requires to find vectors $\mathbf{v}$ such that the matrix multiplication only changes the length of the vector (multiplication by the constant $\lambda$), but not its direction. The number $\lambda$ is called eigenvalue. In general, the eigenvalues are found from the equation $\det(A - \lambda) = 0$, where $\det$ is the determinant, $\det = b_{11}b_{22} - b_{12}b_{21}$. This gives the two solutions

$$\lambda_{\pm} = \frac{a_{11} + a_{22}}{2} \pm \sqrt{a_{12}a_{21} + \frac{1}{4}(a_{11} - a_{22})^2}. \quad (16.52)$$

The corresponding eigenvectors can be written as

$$\mathbf{v}_{\pm} = \begin{pmatrix} a_{12} \\ \lambda_{\pm} - a_{11} \end{pmatrix}. \qquad (16.53)$$

## 6. Revision Quiz

For

$$\mathbf{v} = \begin{pmatrix} 3 \\ 2i \end{pmatrix}, \quad \mathbf{w} = \begin{pmatrix} 2 \\ -i \end{pmatrix}, \quad A = \begin{pmatrix} 1 & i \\ -i & 1 \end{pmatrix}, \quad B = \begin{pmatrix} 1 & i \\ 2 & 2 \end{pmatrix},$$

calculate
  (i) $\mathbf{v} + \mathbf{w}$,
  (ii) $2\mathbf{v} + 3i\mathbf{w}$,
  (iii) $\langle \mathbf{v}|\mathbf{v} \rangle$,
  (iv) $\langle \mathbf{v}|\mathbf{w} \rangle$,
  (v) $A\mathbf{v}$,
  (vi) $B\mathbf{w}$,
  (vii) the eigenvalues and eigenvectors of $A$.

## XVII. HYDROGEN ATOM

The Hydrogen atom consists of an electron of mass $m_e$ and negative charge $-e$, and a nucleus, which is a proton of positive charge $e$ and mass $m_p \approx 1836 m_e$. The total Hamiltonian of electron and proton is given by

$$\hat{H} = \frac{\hat{\mathbf{p}}_p^2}{2m_p} + \frac{\hat{\mathbf{p}}_e^2}{2m_e} - \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_e - \mathbf{r}_p|}, \qquad (17.1)$$

where the potential energy is the Coulomb energy of the two attracting charges.

### A. Separation of relative and centre-of-mass motion

We introduce the centre-of-mass coordinate $\mathbf{R} = \frac{m_e\mathbf{r}_e + m_p\mathbf{r}_p}{m_e + m_p}$ and the relative coordinate $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_p$. The Hamiltonian then takes the form

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}|}, \qquad (17.2)$$

where $\hat{\mathbf{P}} = \hat{\mathbf{p}}_p + \hat{\mathbf{p}}_e$ is the total momentum, $M = m_e + m_p$ is the total mass, $\hat{\mathbf{p}} = \frac{m_e\mathbf{P}_e - m_p\mathbf{P}_p}{m_e + m_p}$ is the momentum of the relative motion, and $\mu = \frac{m_e m_p}{m_e + m_p}$ is the reduced mass. Since $m_e \ll m_p$, $\mu \approx m_e$. We consider the atom at rest, $\mathbf{P} = 0$. Then we have to solve the Schrödinger equation

$$E\psi(\mathbf{r}) = -\frac{\hbar^2}{2\mu}\Delta\psi(\mathbf{r}) - \frac{e^2}{4\pi\varepsilon_0 r}\psi(\mathbf{r}). \qquad (17.3)$$

### B. Separation of radial and angular motion

The Coulomb potential only depends on $r$ and hence is a central potential. Therefore, the solutions of the Schrödinger equation are of the form

$$\psi_{nml}(\mathbf{r}) = R_n(r)Y_{lm}(\theta, \phi), \qquad (17.4)$$

where $Y_{lm}(\theta, \phi)$ are the spherical harmonics of Eq. (14.10).

### C. Radial motion

The radial equation (14.9) now takes the form

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right)R = ER(r). \qquad (17.5)$$

We introduce the rescaled radial coordinate

$$\rho = \sqrt{\frac{-8\mu E}{\hbar^2}}r \qquad (17.6)$$

and the new parameter

$$n = \sqrt{\frac{-\mu}{2E}} \frac{e^2}{4\pi\varepsilon_0\hbar} \qquad (17.7)$$

and look for solutions $R(r) = F(\rho)e^{-\rho/2}$. Equation (17.5) then takes the form

$$\frac{d^2F}{d\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{dF}{d\rho} + \left(\frac{n-1}{\rho} - \frac{l(l+1)}{\rho^2}\right)F = 0. \qquad (17.8)$$

This equation is known as Kummer's differential equation. For integer values $n = l+1, l+2, l+3, \ldots$, the solutions are given by $F_{n,l}(\rho) = \rho^l L_{n-l-1}^{2l+1}(\rho)$, where $L_s^k(\rho)$ are the Laguerre polynomials:

$$L_s^0(\rho) = e^\rho \frac{d^s}{d\rho^s}(e^{-\rho}\rho^s), \quad L_s^k(\rho) = (-1)^k \frac{d^k}{d\rho^k}L_{s+k}^0(\rho). \qquad (17.9)$$

## D. Energies

Since $n = \sqrt{\frac{-\mu}{2E}} \frac{e^2}{4\pi\varepsilon_0\hbar}$ the energy levels of the Hydrogen atom only depend on the *principal quantum number* $n$ but not on $l$ or $m$:

$$E_n = -\frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2 \frac{1}{n^2}. \qquad (17.10)$$

The energies can also be written as $E_n = -\text{Ry}\frac{1}{n^2}$ where $\text{Ry} = \frac{e^2}{8\pi\epsilon_0 a_0} = 13.6$ eV is the so-called Rydberg energy and $a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \approx 0.53\times10^{-10}$m is called the Bohr radius.

The lowest energy level has energy $E_1 = -\text{Ry} = -13.6$ eV. For energy $E > 0$, the electrons are not bound to the nucleus. Hence the Rydberg energy is the amount of energy required to release the electron from the nucleus (this process is called ionisation).

## E. Spectral lines

The electron can change from one energy level $n$ to another level $n'$ if it absorbs or emits a photon which carries the right amount of energy $\hbar\omega = E_n - E_{n'}$. This gives rise to discrete spectral lines. The most important lines are grouped into series, such as the Lyman series ($n' = 1$), the Balmer series ($n' = 2$), and the Paschen series ($n' = 3$).

## F. Degeneracy

For each $n$ the allowed values of $l$ are $0, 1, 2, \ldots, n-1$, and for each $l$ there are $2l+1$ allowed values of $m$. Hence, the degeneracy of each
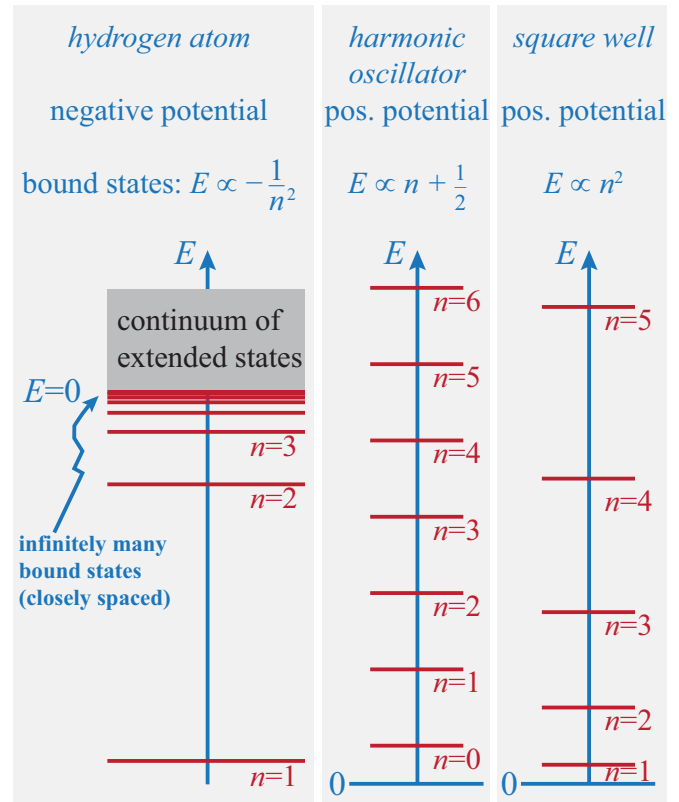


FIG. 8 Comparison of energy levels in three quantum systems.

energy level $E_n$ is $\sum_{l=1}^{n-1}(2l+1) = n^2$. Later we will learn that the electron has an intrinsic degree of freedom called spin so that the degeneracy of each energy level is really $2n^2$. On the other hand we neglected small perturbations which lift the degeneracy and result in a *fine structure* of the energy levels. They will be discussed in the third year module PHYS321, Atomic & Nuclear Physics.

## G. Atomic orbitals

The wavefunctions

$$\psi_{nlm}(\mathbf{r}) = c_{nl}Y_{lm}(\theta,\phi)L_{n-l-1}^{2l+1}(2r/(na_0))r^l e^{-r/(na_0)} \qquad (17.11)$$

of the hydrogen atom are also called atomic orbitals. They are normalised for $c_{nl} = (2/(na_0))^{l+3/2}\sqrt{(n-l-1)!/[2n(n+l)!]}$. The azimuthal quantum number is denoted by a symbol s for $l = 0$, p for $l = 1$, d for $l = 2$, and f for $l = 3$. These symbols are then preceded by the principal wavenumber $n$, so that orbitals are denoted by 1s, 2s, 2p, 3s, 3p, 3d etc.
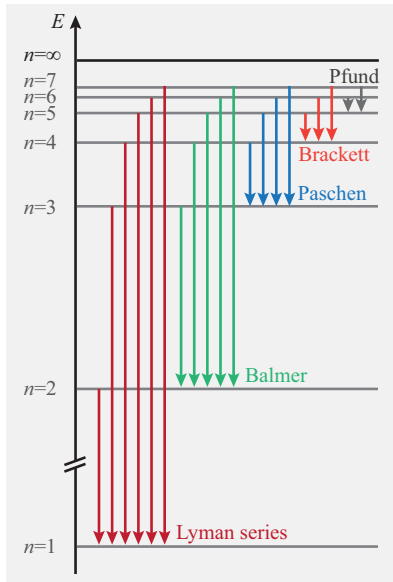
FIG. 9 Spectral series of the hydrogen atom.

### 1. Ground state

The ground state is associated with the spherically symmetric orbital 1s with energy $E_1 = -\mathrm{Ry}$,

$$\psi_{100}(\mathbf{r}) = \sqrt{\frac{1}{\pi a_0^3}}\, e^{-r/a_0}. \qquad (17.12)$$

The probability density to find the particle in a shell of width $dr$ at distance $r$ is given by

$$P(r) = 4\pi r^2 |\psi_{100}(\mathbf{r})|^2 = \frac{4r^2}{a_0^3}e^{-2r/a_0}. \qquad (17.13)$$

This probability density is maximal at $r = a_0$.
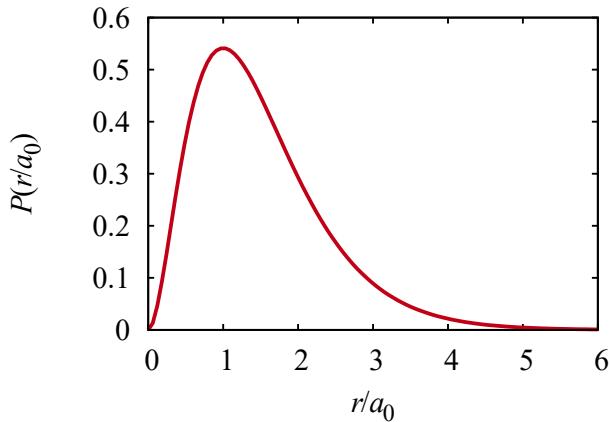


FIG. 10 Radial probability density in the ground state of the hydrogen atom (in units of the Bohr radius $a_0$).

### 2. First excited state

The first excited state has energy $E_2 = -\mathrm{Ry}/4$ and is fourfold degenerate. It consists of the one 2s orbital and three 2p orbitals. The 2s orbital ($l = 0$, $m = 0$) is spherical symmetric,

$$\psi_{200}(\mathbf{r}) = \sqrt{\frac{1}{8\pi a_0^3}} \left(1 - \frac{r}{2a_0}\right) e^{-r/(2a_0)}. \qquad (17.14)$$

The 2p orbitals are not spherical symmetric,

$$\psi_{210}(\mathbf{r}) = \sqrt{\frac{1}{32\pi a_0^3}} \frac{r}{a_0} \cos\theta e^{-r/(2a_0)}, \qquad (17.15)$$

$$\psi_{21,\pm 1}(\mathbf{r}) = \pm\sqrt{\frac{1}{64\pi a_0^3}} \frac{r}{a_0} \sin\theta e^{-r/(2a_0)\pm i\phi}. \qquad (17.16)$$

### 3. Second excited state

The second excited state has energy $E_3 = -\mathrm{Ry}/9$ and is nine-fold degenerate. It consists of one 3s orbital, three 3p orbitals and five 3d orbitals.

### 4. Pictures of atomic orbitals

Figure 11 depicts surfaces of constant probability density for the lowest orbitals of the hydrogen atom.
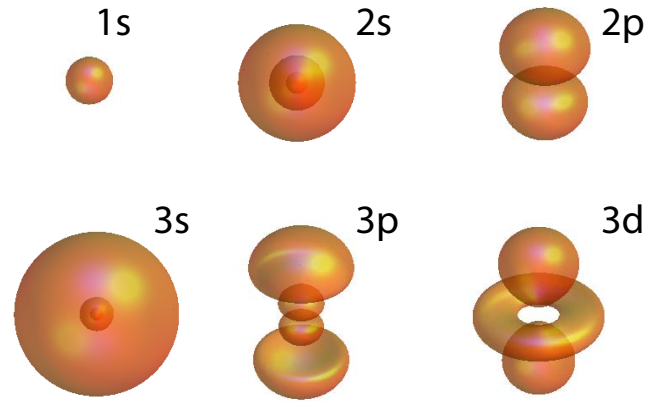


FIG. 11 Equiprobability surfaces of hydrogen orbitals.

## H. Application: The Zeeman effect

We consider the hydrogen atom in a constant magnetic field $\mathbf{B} = B_z \mathbf{k}$, which points into the $z$

direction. The total magnetic moment of the electron is [see Eqs. (15.16) and (16.2)]

$$\hat{\mathbf{m}} = -\frac{e}{2m_e}(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}). \qquad (17.17)$$

The interaction energy of the magnetic moment with the magnetic field is

$$\hat{V}_B = -\mathbf{B} \cdot \hat{\mathbf{m}} = \frac{eB_z}{2m_e}(\hat{L}_z + 2\hat{S}_z). \qquad (17.18)$$

The total Hamiltonian is given by

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}|} + \hat{V}_B. \qquad (17.19)$$

The Schrödinger equation $E\psi = H\psi$ is solved by

$$\psi_{nml\uparrow} = \psi_{nml}(\mathbf{r})\begin{pmatrix}1\\0\end{pmatrix}, \quad (m_s = 1/2) \qquad (17.20)$$

$$\psi_{nml\downarrow} = \psi_{nml}(\mathbf{r})\begin{pmatrix}0\\1\end{pmatrix}, \quad (m_s = -1/2). \qquad (17.21)$$

where $\psi_{nml}(\mathbf{r})$ are the orbital wavefunctions of the hydrogen atom. These functions are eigenfunctions of $\hat{V}_B$:

$$\hat{V}_B\psi_{nml,m_s}(\mathbf{r}) = (m + 2m_s)\mu_B B_z\psi_{nml,m_s}(\mathbf{r}), \qquad (17.22)$$

where $\mu_B = e\hbar/2m_e$ is the Bohr magneton. However, the degeneracy of the eigenvalues is now lifted,

$$E_{nml} = -\frac{e^2}{8\pi\epsilon_0 a_0}\frac{1}{n^2} + (m + 2m_s)\mu_B B_z. \qquad (17.23)$$

The splitting of the levels depends linearly on the strength $B_z$ of the magnetic field.
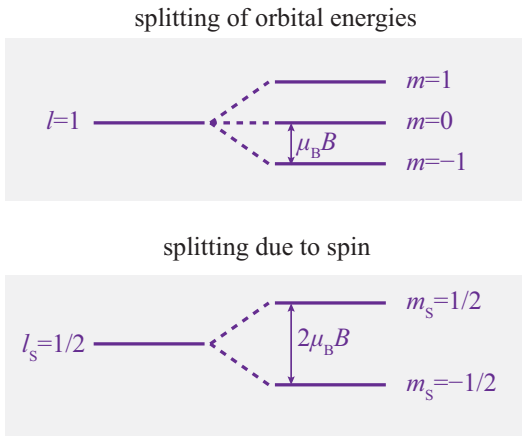


FIG. 12 Level splitting due to Zeeman energy.

The splitting of the orbital energies can be observed in the spectral lines of the hydrogen atom. This is called the Zeeman effect. The observable

spectral lines is restricted by selection rules: $m$ can only change by $-1$, $0$, or $1$, because of properties of the emitted photons. Since $m_s$ cannot change, the spin splitting is not observed in the normal Zeeman effect.



FIG. 13 Normal Zeeman effect.

## XVIII. DYNAMICS FOR STATIONARY HAMILTONIANS

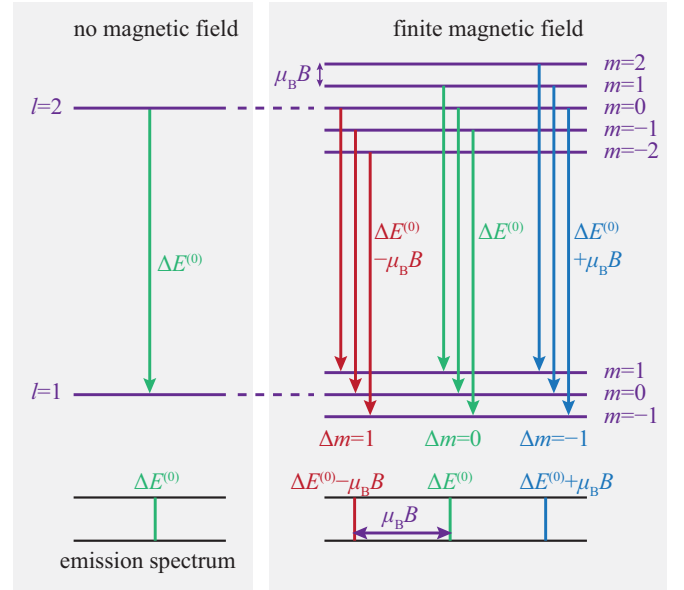According to the postulates of quantum mechanics, the dynamics of a quantum system is encoded in a quantum state $\Psi(t)$ whose time-dependence is determined by the Schrödinger equation

$$i\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle. \tag{18.1}$$

So far in this course we considered quantum systems with time-independent Hamiltonian $\hat{H}$, for which we could use the method of separation of variables to reduce the problem to the stationary Schrödinger equation

$$E_n|\psi_n\rangle = \hat{H}|\psi_n\rangle, \tag{18.2}$$

i.e., we determined the eigenstates $|\psi_n\rangle$ and eigenvalues $E_n$ of $\hat{H}$. In this chapter, we first reconstruct the full time dynamics for such stationary problems, and discuss the ensuing dynamics for some examples.

### A. General solution via eigenstates

The derivation of the stationary Schrödinger equation for time-independent Hamiltonians $\hat{H}$ is based on the trial solution

$$|\Psi_n(t)\rangle = \exp(-iE_nt/\hbar)|\psi_n\rangle. \tag{18.3}$$

We insert this into the time-dependent Schrödinger equation (18.1), which gives

$$E_n|\psi_n\rangle\exp(-iE_nt/\hbar) = \hat{H}|\psi_n\rangle\exp(-iE_nt/\hbar). \tag{18.4}$$

The common factor $\exp(-iE_nt/\hbar)$ on both sides never vanishes, and thus can be divided out; what remains is the stationary Schrödinger equation (18.2).

In order to obtain a general solution of the time-dependent Schrödinger equation (18.1) we should note that this is still a linear differential equation, and thus obeys the superposition principle. Therefore, we can construct new solutions by adding different trial solutions (even if they correspond to different energies): the sum

$$|\Psi(t)\rangle = \sum_n c_n\exp(-iE_nt/\hbar)|\psi_n\rangle \tag{18.5}$$

is still a solution, where the complex constants $c_n$ can be chosen arbitrarily. Here we assumed that the energies $E_n$ are discrete. For continuous energies, the sum is replaced by an integral,

$$|\Psi(t)\rangle = \int dE\, c(E)\exp(-iEt/\hbar)|\psi_E\rangle. \tag{18.6}$$

If both types of spectra coexist (like, e.g., in the hydrogen atom, where we have a discrete set of bound states for $E < 0$, and a continuum of extended states with $E > 0$), we can write

$$|\Psi(t)\rangle = \int dE\, c(E)\exp(-iEt/\hbar)|\psi_E\rangle$$
$$+ \sum_n c_n\exp(-iE_nt/\hbar)|\psi_n\rangle. \tag{18.7}$$

This expression covers all valid solutions of the time-dependent Schrödinger equation with time-independent Hamiltonian.

In practice, we often know the state $|\Psi(t_0)\rangle \equiv |\Psi_0\rangle$ of the quantum system at some time $t_0$. In that case, the specific solution of the Schrödinger equation follows from Eq. (18.7) by a particular choice of the constants $c_n$ and $c_E$. Since the collection of states $\psi_n$, $\psi_E$ form an orthonormal basis, the coefficients can be obtained by evaluating the scalar product,

$$c_n = \exp(iE_nt_0/\hbar)\langle\psi_n|\Psi_0\rangle, \tag{18.8}$$
$$c(E) = \exp(iEt_0/\hbar)\langle\psi_E|\Psi_0\rangle. \tag{18.9}$$

Here, we assumed that the states of the continuous spectrum fulfill the orthonormalisation condition

$$\langle\psi_{E'}|\psi_E\rangle = \delta(E' - E), \tag{18.10}$$

where $\delta$ is the *Dirac delta function*, defined by $\int_{-\infty}^{\infty}\delta(x)f(x)\,dx = f(0)$.

The expansion coefficients $c_n$ determine the probability to find the system in the discrete bound state with energy $E_n$, while $c(E)$ determines the probability density of the extended energy eigenstates in the continuous part of the spectrum:

$$P(E_n) = |c_n|^2, \quad P(E) = |c(E)|^2. \tag{18.11}$$

These probabilities are independent of time, which is a consequence of *energy conservation* in stationary quantum systems. The expectation value of the energy follows from the general solution (18.7),

$$\langle\Psi(t)|\hat{H}\Psi(t)\rangle = \sum_n E_n|c_n|^2 + \int dE\, E|c(E)|^2. \tag{18.12}$$

In the following, we formulate expressions only using the symbols for a discrete spectrum (quantities $c_n$, $E_n$, $|\psi_n\rangle$, $\psi_n(x)$, etc.), but imply that these have to be replaced by their continuous counterparts (with the sum $\sum_n$ replaced by integration over energy) if the spectrum is continuous.

## B. General solution via the time-evolution operator

The approach above requires to determine all eigenstates of the system, and to match the initial condition $|\Psi(t_0)\rangle$ to a superposition of these states. In many cases, a more formal approach proves advantageous: We seek an operator $\hat{U}(t - t_0)$ such that

$$|\Psi(t)\rangle = \hat{U}(t - t_0)|\Psi(t_0)\rangle. \qquad (18.13)$$

The operator $\hat{U}(t)$ is known as the *time-evolution operator*. The linearity of the time-dependent Schrödinger equation guarantees that this operator is linear, too. Indeed, we can give a formal (but often also practically useful) expression which relates $\hat{U}$ directly to the Hamiltonian:

$$\hat{U}(t) = \exp(-i\hat{H}t/\hbar). \qquad (18.14)$$

The right-hand side has to be interpreted as a Taylor expansion; for any operator $\hat{A}$, $\exp(\hat{A}) = \sum_{n=0}^{\infty} \hat{A}^n/n!$. This can be used to show

$$\frac{d}{dt}\hat{U}(t) = -\frac{i}{\hbar}\hat{H}\hat{U}(t), \qquad (18.15)$$

where the derivative of an operator $\hat{A}(t)$ is defined as $\frac{d}{dt}\hat{A}(t) = \lim_{\varepsilon \to 0} \varepsilon^{-1}[\hat{A}(t + \varepsilon) - \hat{A}(t)]$. The validity of Eq. (18.14) then follows by inserting Eq. (18.13) into the time-dependent Schrödinger equation (18.1). The initial condition is verified by observing

$$\hat{U}(0) = \hat{I}, \qquad (18.16)$$

where $\hat{I}$ is the identity operator ($\hat{I}|\psi\rangle = |\psi\rangle$ for all $|\psi\rangle$).

It directly follows from Eq. (18.14) that $\hat{U}$ is unitary:

$$\hat{U}^{-1}(t) = \hat{U}(-t) = \exp(i\hat{H}t/\hbar) = \hat{U}^{\dagger}(t), \qquad (18.17)$$

where we used in the last step that $\hat{H}$ is hermitian. Importantly, this guarantees that an initially normalised state $|\Psi(t)\rangle$ remains normalised during the time evolution.

## C. Example I: Dynamics of the free particle

As a first example, we study the case of a free particle in one dimension, for which the stationary Schrödinger equation

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) \qquad (18.18)$$

is solved by the momentum eigenfunctions

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}\exp(ipx/\hbar), \qquad (18.19)$$

with energy given by $E_p = p^2/2m$. Therefore, the partial solutions of the time-dependent Schrödinger equation are plane propagating waves

$$\Psi_p(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\exp(ipx/\hbar - iE_pt/\hbar). \qquad (18.20)$$

Assume that at time $t_0 = 0$ the system is in a state $\psi(x)$, expressed as a superposition of plane waves

$$\psi(x) = \int_{-\infty}^{\infty} dp\, \tilde{\psi}(p)\psi_p(x). \qquad (18.21)$$

The expansion coefficients

$$\tilde{\psi}(p) = \langle \psi_p|\psi \rangle = \int_{-\infty}^{\infty} dx\, \psi_p^*(x)\psi(x) \qquad (18.22)$$

follow from the Fourier transformation of the initial state, and are identical to the momentum wave function introduced in section VII.A. The time-dependent state is then given by

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} dp\, \tilde{\psi}(p)\exp(ipx/\hbar - iE_pt/\hbar). \qquad (18.23)$$

We can also write this as

$$\Psi(x,t) = \int_{-\infty}^{\infty} dp\, \tilde{\Psi}(p,t)\psi_p(x), \qquad (18.24)$$

i.e., as a Fourier transformation with time-dependent coefficients

$$\tilde{\Psi}(p,t) = \tilde{\psi}(p)\exp(-iE_pt/\hbar). \qquad (18.25)$$

In terms of this *time-dependent momentum wave function*, the probability density for momentum is given by $P(p,t) = |\tilde{\Psi}(p,t)|^2$. For the free particle, the probability density is stationary, $P(p,t) = |\tilde{\psi}(p)|^2$, which is a consequence of momentum conservation in absence of forces acting on the particle.

In order to get some insight into the time dependence of the position wave function, let us consider the case of a particle initially described by a wave packet centred at $x_0 = 0$,

$$\psi(x) = (2\pi\sigma^2)^{-1/4}\exp(-x^2/4\sigma^2 + ip_0x/\hbar), \qquad (18.26)$$

where $\sigma$ and $p_0$ are constants. As shown in section VII.E, this wave packet has expectation values $\langle x \rangle = 0$ and $\langle p \rangle = p_0$, as well as uncertainties $\Delta x = \sigma$ and $\Delta p = \hbar/2\sigma$. We have also calculated the corresponding momentum wave function

$$\tilde{\psi}(p) = (2\sigma^2/\hbar^2\pi)^{1/4}\exp[-\sigma^2(p - p_0)^2/\hbar^2]. \qquad (18.27)$$

Equation (18.23) for the time-dependent wave function then reduces to a (complex) Gaussian integral, which can be solved analytically. The results can be written as a generalised wave packet

of the form

$$\Psi(x,t) = (2\pi\sigma_t^2)^{-1/4} \exp\left[-\frac{(x-p_0t/m)^2}{4|\sigma_t|^2}\right]$$
$$\times \exp\left[i\frac{\sigma^2}{|\sigma_t|^2}\left(\frac{p_0 x}{\hbar} - \frac{p_0^2 t}{2m\hbar} + \frac{x^2\hbar t}{8m\sigma^4}\right)\right],$$
(18.28)

where $\sigma_t = \sigma + (i\hbar/2m\sigma)t$. The position probability density

$$P(x,t) = (2\pi|\sigma_t|^2)^{-1/2}\exp\left[-\frac{(x-p_0t/m)^2}{2|\sigma_t|^2}\right] \quad (18.29)$$

is still a Gaussian, with a linearly drifting expectation value $\langle x \rangle = p_0 t/m$, and an uncertainty $\Delta x = |\sigma_t| = \sigma\sqrt{1 + (\hbar^2/4m^2\sigma^4)t^2}$ which increases slowly as long as $t \ll m\sigma^2/\hbar$.

### D. Detour: the time of flight

Classically, the momentum of a free particle can be measured in a *time-of-flight experiment*, where one observes the particle's positions $x_0$ and $x$ at times $t_0$ and $t$, and evaluates $p = m(x-x_0)/(t-t_0)$. Quantum mechanically, we cannot know position and momentum at the time. As we now demonstrate, it is still instructive to carry out such a momentum measurement. The main requirement for its accuracy is to choose $t - t_0$ sufficiently large, so that the position probability spreads out over a large region in space (therefore, the measurement remains in accordance with the uncertainty principle).

In order to see how this works, let us set $t_0 = 0$ and assume that the particle is initially localised around position $x_0 = 0$, which can be enforced in practice by confining the particle in a suitable potential. We denote the corresponding wave function by $\psi(x)$, but don't require this to be a Gaussian wave packet. Because $\psi(x)$ is well localised, we can assume (again in accordance with the uncertainty principle) that the associated momentum wave function $\tilde{\psi}(p)$ is rather smooth.

Next, we let the particle move freely (in the practical setting above, we switch off the confining potential). For large times, the time-evolved wave function (18.23) can be approximated using an advanced mathematical method, known as the *stationary phase approximation*. The idea behind this approximation is to observe that for large $t$, the function $S(x) \equiv px - p^2t/2m$ in the exponent of the integrand changes rapidly as a function of the integration variable $p$. Therefore, the integrand oscillates wildly, and tends to average out. The only exceptions are the vicinities of values $p_s$ of $p$ where

the function $S(x)$ is stationary, i.e., has a vanishing derivative. Here, this is the case for $p_s = mx/t$. In the vicinity of this *stationary point* the integral can be approximated by a complex Gaussian. The result of this approximation is

$$\Psi(x,t) \approx \sqrt{m/t}\tilde{\psi}(mx/t)\exp\left(i\frac{x^2m}{2t\hbar} - i\frac{\pi}{4}\right). \quad (18.30)$$

Therefore, the position probability density at time $t$ is

$$P(x,t) \approx \frac{m}{t}|\tilde{\psi}(mx/t)|^2. \quad (18.31)$$

This can be translated into a probability distribution of the momentum $p = mx/t$:

$$P(p) = P(x,t)\frac{dx}{dp} = |\tilde{\psi}(p)|. \quad (18.32)$$

In this way, we recover our original interpretation of the momentum wave function! Note that at large times, the initial wave packet has spread out over a large region in space; this counteracts the increasing accuracy of this momentum measurement, in accordance with the uncertainty principle.

### E. Example II: coherent state dynamics in the harmonic oscillator

Interestingly, with suitable initial conditions the quantum dynamics of the harmonic oscillator turns out to be somewhat simpler than that of the free particle. This is realised when the initial wavefunction corresponds to the *displaced* ground state wave function (a so-called *coherent state*)

$$\psi(x) = \psi_0(x - X_0) = (2\pi\sigma^2)^{-1/4}\exp[-(x-X_0)^2/4\sigma^2],$$
(18.33)

where $\sigma^2 = \hbar/2m\omega$, and $X_0$ is a constant. The time-dependent solution can then be found from the ansatz

$$\Psi(x,t) = \psi_0(x-X(t))\exp[ixP(t)/\hbar + iS(t)/\hbar], \quad (18.34)$$

where $X(t)$, $P(t)$, and $S(t)$ are functions of time. We insert this into the time-dependent Schrödinger equation and compare both sides to obtain

$$[-im\omega X\dot{X} - \dot{S}] + x\{-\dot{P} + im\omega\dot{X}\}$$
$$= \left[\frac{\hbar\omega}{2} + \frac{P^2}{2m} - \frac{m\omega^2}{2}X^2 - iPX\omega\right] + x\{m\omega^2 X + iP\omega\},$$
(18.35)

where we suppressed the argument $t$ of $X$ and $P$, and used a dot to denote time derivatives. Comparing the real and imaginary parts in the curly brackets we find

$$\dot{P} = -m\omega^2 X, \quad \dot{X} = P/m, \quad (18.36)$$

which are just the classical equations of motion for the oscillator. The solution for initial conditions $X(0) = X_0$, $P(0) = 0$ is given by

$$X(t) = X_0 \cos(\omega t), \quad P(t) = -m\omega X_0 \sin(\omega t). \quad (18.37)$$

We now can obtain $S$ by comparing the bracketed terms in Eq. (18.35), which demands

$$\dot{S} = -\frac{\hbar\omega + \dot{X}P + \dot{P}X}{2} \Rightarrow S(t) = -\frac{\hbar\omega t + P(t)X(t)}{2}. \quad (18.38)$$

The time-dependent solution $\Psi(x,y)$ follows by inserting these expressions in Eq. (18.34). This allows to determine the associated expectation values $\langle x \rangle = X(t)$ of position and $\langle p \rangle = P(t)$ of momentum, which therefore follow the classical motion (this is a consequence of the *Ehrenfest theorem*, which establishes a similar relation for arbitrary quantum systems). Furthermore, the uncertainties $\Delta x = \sigma$ and $\Delta p = \hbar/2\sigma$ are time-independent. Therefore, the motion of this wave packet mimics the classical motion as closely as it is possible under the constraints of the uncertainty principle.

The expectation value of energy

$$\langle \hat{H} \rangle = \hbar\omega/2 + P^2(t)/2m + m\omega^2 X^2(t)/2 \quad (18.39)$$
$$= \hbar\omega/2 + m\omega^2 X_0^2/2 \quad (18.40)$$

is also time-independent, but this is simply a consequence of energy conservation in stationary problems. Compared to the classical expression, we encounter an additional positive contribution $\hbar\omega/2$, the ground state energy, which we associated with the zero-point motion enforced by the uncertainty principle.

## F. Example III: Spin precession (dynamics of a two-state system)

A large range of quantum problems only involves a pair of quantum states, either exactly as for the spin of an electron, or approximately because other states are energetically unaccessible and therefore can be neglected. Examples of the latter situation are the dynamics in the ground and first excited state of an atom at low energies, or the low-energy dynamics of a particle in a symmetric double-well potential. In all these cases, we can reduce the wave function to a two-component vector $\psi = \binom{\alpha}{\beta}$, where the two components determine the probabilities $P_1 = |\alpha|^2$, $P_2 = |\beta|^2$ to find the system in state $\binom{1}{0}$ or $\binom{0}{1}$, respectively.

We remind ourselves of the 3-dimensional real *polarisation vector*

$$\vec{P} = (\langle \sigma_x \rangle, \langle \sigma_y \rangle, \langle \sigma_z \rangle) \quad (18.41)$$
$$= (2\operatorname{Re}\alpha^*\beta, 2\operatorname{Im}\alpha^*\beta, |\alpha|^2 - |\beta|^2), \quad (18.42)$$

where $\sigma_x$, $\sigma_y$, and $\sigma_z$ are the three Pauli matrices which we introduced for the description of the electronic spin. If $\psi$ is normalised then the polarisation vector is of unit length, i.e., it is restricted to the surface of a sphere, the so-called *Bloch sphere*.

Linear operators $\hat{A}$ acting on two-component states $\psi$ are of the form of a $2 \times 2$-dimensional matrix. These can be expressed as a sum

$$\hat{A} = a_0 I + a_x \sigma_x + a_y \sigma_y + a_z \sigma_z, \quad (18.43)$$

where $I$ is the $2 \times 2$-dimensional identity matrix. For hermitian operators, the coefficients $a_{0,x,y,z}$ are all real. Furthermore, any unitary operator can also be written formally as

$$\hat{U} = \exp[-i\varphi(n_x\sigma_x + n_y\sigma_x + n_z\sigma_x)/2]e^{i\chi} \quad (18.44)$$
$$= \cos(\varphi/2)e^{i\chi}I - i\sin(\varphi/2)e^{i\chi}(n_x\sigma_x + n_y\sigma_y + n_z\sigma_z), \quad (18.45)$$

where we assume $n_x^2 + n_y^2 + n_z^2 = 1$. (The expression on the second line follows directly from the Taylor-series definition of the exponential function.) By examining the polarisation vector of the state $\hat{U}\psi$ one finds that $\hat{U}$ induces a rigid rotation of the Bloch sphere, by an angle $\varphi$ about the axis $\mathbf{n} = n_x\mathbf{i} + n_y\mathbf{j} + n_z\mathbf{k}$.

We now use these general features of two-component vectors and matrices to examine the dynamics of a two-state system, based on a time-independent Hamiltonian of the form

$$H = a_x \sigma_x + a_y \sigma_y + a_z \sigma_z \quad (18.46)$$

where the three coefficients are all real and time-independent. (We set $a_0 = 0$ since this simply shifts the energy. For an electronic spin, this Hamiltonian can be realised by applying a magnetic field of suitable strength $B$ into the direction $\mathbf{n}$ of the vector $\mathbf{a} = a_x\mathbf{i} + a_y\mathbf{j} + a_z\mathbf{k} = a\mathbf{n}$, which then is given by $\mathbf{a} = \frac{g_e e\hbar}{4m_e}\mathbf{B}$ where $g_e \approx 2$ is the *g-factor*.) A general solution of this problem is provided by the time-evolution operator

$$\hat{U}(t) = \exp(-i\hat{H}t/\hbar) \quad (18.47)$$
$$= \exp[-i\omega t(n_x\sigma_x + n_y\sigma_y + n_z\sigma_z)/2] \quad (18.48)$$

where $\omega = (2a/\hbar)$ is known as the *Larmor frequency*. (For an electronic spin in a magnetic field, $\omega = \frac{g_e eB}{2m_e}$.) Being unitary, the time-evolution operator can be cast into the form Eq. (18.44), which here simply amounts to equating $\varphi = \omega t$ and $\chi = 0$, while $\mathbf{n}$ remains fixed. Therefore, the dynamics corresponds to a permanent rotation of the Bloch sphere about the axis $\mathbf{n}$, with angular frequency $\omega$. This motion, known as *Larmor precession*, is analogous to the precession of a rotating top under the influence of gravity.

In order to get further insight into the dynamics (and illustrate the solution method based on the eigenstates of the stationary Schrödinger equation), we now specialise to the case of a Hamiltonian

$$H = -\frac{\Delta}{2}\sigma_x = \begin{pmatrix} 0 & -\Delta/2 \\ -\Delta/2 & 0 \end{pmatrix}, \qquad (18.49)$$

where we have expressed the coefficient $a_x$ in terms of a suitable constant $\Delta$ whose meaning will become clear shortly. For a spin, this Hamiltonian can be realised by applying a magnetic field into the $x$ direction. For the double well, $\Delta$ is associated with the tunneling between the troughs.

The stationary Schrödinger equation $E\psi = H\psi$ is solved by the eigenvectors $\psi_+ = 2^{-1/2}\binom{1}{1}$ (the *symmetric* state, with energy $-\Delta/2$) and $\psi_- = 2^{-1/2}\binom{1}{-1}$ (the *antisymmetric* state, with energy $\Delta/2$). Therefore, $\Delta$ amounts to the energy difference between the two states (in the context of the double well, this is also known as the *tunnel splitting*).

We now can use Eq. (18.5) to construct the time-dependent state

$$\Psi(t) = a_+ \exp(i\Delta t/2\hbar)\psi_+ + a_- \exp(-i\Delta t/2\hbar)\psi_-, \qquad (18.50)$$

where $a_-$ and $a_+$ are determined by the initial conditions $\psi(0)$. The state is normalised for $|a_+|^2 + |a_-|^2 = 1$.

Let us assume that the system is initially in the state $\psi(0) = \binom{1}{0}$. Then the solution of the Schrödinger equation is

$$\psi(t) = \begin{pmatrix} \cos(\Delta t/2\hbar) \\ i\sin(\Delta t/2\hbar) \end{pmatrix}. \qquad (18.51)$$

This gives the probability $P_1 = \cos^2(\Delta t/2\hbar) = \frac{1}{2}[1 + \cos(\Delta t/\hbar)]$ that the system occupies the state $\binom{1}{0}$ and $P_2 = \sin^2(\Delta t/2\hbar) = \frac{1}{2}[1 - \cos(\Delta t/\hbar)]$ that the system occupies the state $\binom{0}{1}$.

Hence the quantum system oscillates between the states $\binom{1}{0}$ and $\binom{0}{1}$. The oscillation is periodic, $P_1(t + T) = P_1(t)$, with period $T = 2\pi\hbar/\Delta$ (corresponding to Larmor frequency $\omega = \Delta/\hbar$). If we wait for half a period, $t = T/2$, the state changes from $\binom{1}{0}$ to $\binom{0}{1}$.

For spin, these oscillations are again interpreted as a *precession* in the magnetic field. For the double well, the oscillations correspond to tunnelling back and forth between the two troughs.

## XIX. DYNAMICS FOR TIME-DEPENDENT HAMILTONIANS

We now turn to the dynamics of quantum systems with a Hamiltonian $\hat{H}(t)$ which itself changes over time. This time dependence is generally induced externally, e.g., by the dynamics in the environment of the system, or when a system is driven by external fields. However, a very similar situation arises if we start with a stationary system but focus on only some of its physical components; the time dependence then arises from the interaction with the rest of the system. Henceforth, we will call systems with time-dependent Hamiltonian *driven*, and refer to the explicit time dependence as the *driving*, irrespective of the actual origin of this time dependence. Our main concern will be to investigate how a time-dependent potential induces *transitions* between quantum states. The starting point will again be the time-dependent Schrödinger equation

$$i\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle. \qquad (19.1)$$

### A. Rabi oscillations

A striking effect induced by driving are *transitions* between quantum levels. Let us consider a harmonically driven two-level system with Hamiltonian

$$\hat{H}(t) = \begin{pmatrix} -\Delta/2 & V\exp(i\omega t) \\ V\exp(-i\omega t) & \Delta/2 \end{pmatrix}, \qquad (19.2)$$

where $V$ is a real constant. In absence of the driving ($V = 0$), the Hamiltonian possesses stationary eigenstates $\psi_1 = \binom{1}{0}$, $\psi_2 = \binom{0}{1}$ with energies $E_1 = -\Delta/2$ and $E_2 = \Delta/2$, respectively, and no transitions occur if the system is placed in one of these states.

For finite $V$, we can find the exact dynamics of the system by stipulating

$$\Psi(t) = \begin{pmatrix} a\exp[i(\Omega + \omega)t/2] \\ b\exp[i(\Omega - \omega)t/2] \end{pmatrix}, \qquad (19.3)$$

where the constants $\Omega$, $a$ and $b$ determine the transition rates and amplitudes between the states $\psi_{1,2}$. These quantities are determined by inserting Eq. (19.3) into the time-dependent Schrödinger equation (19.1), which results in the two equations

$$[-\hbar(\Omega + \omega)/2]a = -(\Delta/2)a + Vb, \qquad (19.4)$$
$$[-\hbar(\Omega - \omega)/2]b = Va + (\Delta/2)b. \qquad (19.5)$$

This homogeneous system with two unknowns $a$, $b$ is only solvable if both equations are linearly dependent, which requires

$$\frac{1}{4}[\hbar(\Omega + \omega) - \Delta][\hbar(\Omega - \omega) + \Delta] - V^2 = 0. \qquad (19.6)$$

There are two solutions,

$$\Omega = \pm\Omega_0, \quad \Omega_0 = \sqrt{(\omega - \Delta/\hbar)^2 + 4V^2/\hbar^2}, \quad (19.7)$$

where $\Omega_0$ is the *Rabi frequency*. The associated amplitudes are

$$a_\pm = 2V, \quad b_\pm = \Delta - \hbar\omega \mp \hbar\Omega_0. \quad (19.8)$$

These two solutions can be superposed to find the full time dependence of the quantum state for arbitrary initial conditions. If the initial state is $\Psi(0) = \psi_1$, then

$$\Psi(t) = \begin{pmatrix} e^{i\omega t/2}\left[\cos\frac{\Omega_0 t}{2} - i\frac{\omega - \Delta/\hbar}{\Omega_0}\sin\frac{\Omega_0 t}{2}\right] \\ -i\frac{2V}{\hbar\Omega_0}e^{-i\omega t/2}\sin\frac{\Omega_0 t}{2} \end{pmatrix}. \quad (19.9)$$

The probabilities for occupation of states 1 and 2 follow as

$$P_1 = 1 - \left(\frac{2V}{\hbar\Omega_0}\right)^2\sin^2\frac{\Omega_0 t}{2}, \quad P_2 = \left(\frac{2V}{\hbar\Omega_0}\right)^2\sin^2\frac{\Omega_0 t}{2}. \quad (19.10)$$

These probabilities vary periodically with the Rabi frequency, which therefore determines the time $T = 2\pi/\Omega_0$ after which the system returns into its initial state. One such period defines a *Rabi cycle*. After half a cycle, the occupation probability of state 2 is maximal. It reaches $P_2 = 1$ is the system is driven at *resonance*, $\omega = \Delta/\hbar$, where the Rabi frequency $\Omega_0 = 2|V|/\hbar$ attains its minimal value. At resonance, the system periodically absorbs and emits an energy $\Delta = \hbar\omega$, in close analogy to the Planck relation.

The Rabi cycle forms the basis of electron spin resonance (ESR), muon spin resonance, and nuclear magnetic resonance (NMR), which are widely used experimental techniques in material science.

## B. General solution via the time-evolution operator

For most driven quantum systems the time-dependent Schrödinger equation (19.1) cannot be solved exactly as in the preceding example. A systematic treatment is still possible in terms of a suitably generalised time-evolution operator $\hat{U}(t, t_0)$, which is obtained by introducing two independent time arguments and stipulating

$$|\Psi(t)\rangle = \hat{U}(t, t_0)|\Psi(t_0)\rangle. \quad (19.11)$$

The time-dependent Schrödinger equation (19.1) then demands that $\hat{U}$ obeys

$$i\hbar\frac{d}{dt}\hat{U}(t, t_0) = \hat{H}(t)\hat{U}(t, t_0), \quad (19.12)$$

which has to be solved with initial condition

$$\hat{U}(t_0, t_0) = \hat{I}. \quad (19.13)$$

The defining property (19.11) entails the multiplication rule $\hat{U}(t, t_0) = \hat{U}(t, t_1)\hat{U}(t_1, t_0)$. This can be used to construct an explicit, but somewhat formal solution of (19.12) which generalizes the expression $\hat{U}(t) = \exp(-i\hat{H}t/\hbar)$ obtained for stationary problems. In order to formulate this solution, we introduce the *time-ordering operator* $\mathcal{T}$, which acts on products of time-dependent operators according to

$$\mathcal{T}\hat{A}(s)\hat{B}(s') = \begin{cases} \hat{A}(s)\hat{B}(s'), & s \geq s' \\ \hat{B}(s')\hat{A}(s), & s < s' \end{cases}. \quad (19.14)$$

This is more accurately termed a superoperator since it doesn't act the the wavefunction but on operators itself; $\mathcal{T}$ takes a product of such operators an shuffles the operator with the latest time argument to the left. We then can write

$$\hat{U}(t, t_0) = \mathcal{T}\exp\left[-\frac{i}{\hbar}\int_{t_0}^t ds\, H(s)\right], \quad (19.15)$$

where $\mathcal{T}$ acts on the terms of the Taylor expansion of the exponential function. This time ordering is enforced because in Eq. (19.12), $\hat{H}(t)$ appears to the left of $\hat{U}(t, t_0)$ where $t$ refers to the latest time during the evolution from $t_0$ to $t$ (note that the operators $\hat{H}(t)$ and $\hat{U}(t, t_0)$ generally don't commute).

While Eq. (19.15) is of some practical use, there exist advanced approaches based on the time evolution operator which circumvent its explicit construction. Among the more notable ones are operator techniques (such as the Heisenberg and interaction pictures), path integrals, and semiclassical approximations. In the following we briefly discuss the Heisenberg picture, and the related Ehrenfest theorem.

## C. Ehrenfest theorem and Heisenberg picture

We start with a general statement about expectation values. Let us consider the expectation value of an observable $\hat{A}$,

$$\langle\Psi(t)|\hat{A}|\Psi(t)\rangle = \langle\Psi(0)|\hat{U}^\dagger(t, 0)\hat{A}\hat{U}(t, 0)|\Psi(0)\rangle, \quad (19.16)$$

and evaluate its time derivative using Eq. (19.12) (the analogous equation for $\hat{U}^\dagger$ follows from taking the hermitian conjugate of this equation). This then delivers the *Ehrenfest theorem*,

$$\frac{d}{dt}\langle\Psi(t)|\hat{A}|\Psi(t)\rangle = \frac{i}{\hbar}\langle\Psi(t)|[\hat{H}, \hat{A}]|\Psi(t)\rangle, \quad (19.17)$$

thus, a relation between the time derivative of the expectation value and an expectation value of a commutator. In some cases, these equations are

formally identical to the classical equations of motion (following from Newton's equation). In general, however, the commutators generate new expressions, giving rise to an infinite hierarchy of equations. This problem can be circumvented by introducing time-dependent operators,

$$\hat{A}(t) = \hat{U}^\dagger(t,0)\hat{A}\hat{U}(t,0), \tag{19.18}$$

which fulfill the Heisenberg equations of motion

$$\frac{d}{dt}\hat{A} = \frac{i}{\hbar}[\hat{H},\hat{A}]. \tag{19.19}$$

Expectation values are then evaluated as

$$\langle\Psi(0)|\hat{A}(t)|\Psi(0)\rangle, \tag{19.20}$$

thus, the Heisenberg picture replaces the time-evolution of the quantum state by time-evolution of operators.

An application of the Ehrenfest theorem and the Heisenberg equations of motion is discussed as a worksheet question.

## D. Time-dependent perturbation theory and Fermi's golden rule

We now revert back to the type of quantum mechanics pursued so far, and discuss the most direct approach to time dependence, time-dependent perturbation theory, which provides estimates of transition rates if the driving is weak.

Time-dependent perturbation theory sets out by separating the stationary parts $\hat{H}_0$ of the Hamiltonian $\hat{H}(t) = \hat{H}_0 + \hat{w}(t)$ from the driving $\hat{w}(t)$. In absence of the driving, the Hamiltonian is stationary and has energies $E_n$ and eigenstates $|\psi_n\rangle$ solving the stationary Schrödinger equation

$$E_n|\psi_n\rangle = \hat{H}_0|\psi_n\rangle. \tag{19.21}$$

In presence of the driving, we use these states and energies to express the quantum state as

$$|\Psi(t)\rangle = \sum_n c_n(t)\exp(-iE_n t/\hbar)|\psi_n\rangle. \tag{19.22}$$

The expansion coefficients $c_n(t)$ determine the probability $P_n(t) = |c_n(t)|^2$ to find the system in the stationary state $|\psi_n\rangle$. At a given time $t_0$, their values can be obtained from the scalar product

$$c_n = \exp(iE_n t_0/\hbar)\langle\psi_n|\Psi_0\rangle. \tag{19.23}$$

The subsequent time dependence of these coefficients follows from the time-dependent Schrödinger equation (19.1):

$$i\hbar\frac{dc_m}{dt} = \sum_n w_{mn}(t)e^{iE_{mn}t/\hbar}c_n(t), \tag{19.24}$$

where $w_{mn}(t) = \langle\psi_m|\hat{w}(t)|\psi_n\rangle$ denotes the time-dependent matrix elements of the driving, and we defined $E_{mn} = E_m - E_n$.

In absence of the driving, the coefficients $c_n$ are constant. If the driving is weak, they only change slowly, and we can approximate $c_n(t) \approx c_n^0$ on the right-hand side of Eq. (19.24). We can then integrate to obtain the *first order of time-dependent perturbation*,

$$c_m(t) \approx c_m^0 + \frac{1}{i\hbar}\int_{t_0}^t \sum_n w_{mn}(\tau)e^{iE_{mn}\tau/\hbar}c_n^0\, d\tau \equiv c_m^{(1)}(t). \tag{19.25}$$

This procedure can be repeated by inserting the improved result $c_n(t) \approx c_n^{(1)}(t)$ into the right-hand side of Eq. (19.24), and integrating again. This delivers the second order of perturbation theory, and in principle can be iterated to successively generate expressions of increasingly high order, as well.

If initially only a single state $n$ is populated [$c_n(t_0) = 1$, $c_m(t_0) = 0$ for $m \neq n$], the first-order result (19.25) estimates the *transition probability* into state $m$ as

$$P_{n\to m}^{(1)} = \frac{1}{\hbar^2}\left|\int_{t_0}^t w_{mn}(\tau)e^{iE_{mn}\tau/\hbar}\, d\tau\right|^2. \tag{19.26}$$

Furthermore, to this level of approximation the amplitude

$$c_n(t) \approx \exp\left[-\frac{i}{\hbar}\int_{t_0}^t w_{nn}(\tau)d\tau\right] \tag{19.27}$$

of the initially populated state only changes its phase.

### 1. Sudden perturbation

Consider a system whose Hamiltonian changes abruptly from $\hat{H} = \hat{H}_0$ for $t < 0$ to $\hat{H} = \hat{H}_0 + \hat{W} \equiv \hat{H}_1$ for $t > 0$, where $\hat{H}_0$ and $\hat{W}$ are time-independent [therefore, $\hat{w}(t) = \hat{W}(t)\Theta(t)$, where $\Theta(t)$ is the unit step function]. This change does not induce any instantaneous jump of the state $|\Psi(t)\rangle$ at $t = 0$, but modifies the subsequent dynamics because the 'old' eigenstates of $|\psi_n^{(0)}\rangle$ and energies $E_n^{(0)}$ of $\hat{H}_0$ differ from the 'new' eigenstates $|\psi_n^{(1)}\rangle$ and energies $E_n^{(1)}$ of $\hat{H}_1$. There are two natural ways to describe the effects of such a sudden approximation:

(i) We can calculate the *overlaps* $d_{mn} = \langle\psi_m^{(1)}|\psi_n^{(0)}\rangle$ between the two sets of eigenstates. These deliver the probabilities $P_{mn} = |d_{mn}|^2$ for transitions from an old eigenstate $|\psi_n^{(0)}\rangle$ to a new eigenstate $|\psi_m^{(1)}\rangle$.

(ii) We can work with the eigenstates $|\psi_n^{(0)}\rangle$ throughout, and examine how their population

changes over time. Using the first-order approximation (19.26), the transition probability is estimated as

$$P_{n\to m}^{(1)} = \frac{2\pi}{\hbar}|\hat{W}_{mn}|^2 \left\{ \frac{2\hbar}{\pi}\frac{\sin^2(E_{mn}t/2\hbar)}{|E_{mn}|^2} \right\}. \quad (19.28)$$

The function in the curly brackets has a maximum around $E_{mn} = 0$, and decays to small values when one deviates by $\Delta E_{mn} \sim \hbar/\Delta t$, in close resemblance to the energy-time uncertainty principle. For sufficiently large times, this function becomes sharply peaked and can be approximated as $t\delta(E_m - E_n)$, where we again encounter Dirac's delta function. Therefore, energy-conserving transitions are favored.

In practical situations, we are often interested in transitions into a continuous set of extended states with $E \approx E_n$ (sometimes further specified by propagation direction into which the system disintegrates, spin, or similar common characteristics of the final states). The delta function is then replaced by the *density* $\rho(E)$ of the final states, and the *transition rate* $\Gamma_n = \sum_m dP_{n\to m}/dt$ into these states can be estimated as

$$\Gamma_n = \frac{2\pi}{\hbar}|\hat{W}_{mn}|^2\rho(E_n), \quad (19.29)$$

where we assume that $W_{mn} \approx \text{const}$ for the specified set of final states. This important expression (first derived by Dirac) is known as *Fermi's golden rule*.

### 2. Harmonic perturbation

Fermi's golden rule can be generalised to the important case of a harmonic perturbation

$$\hat{w}(t) = \hat{W}e^{i\omega t} + \hat{W}^\dagger e^{-i\omega t}, \quad (19.30)$$

where $\hat{W}$ is time-independent. The derivation follows the steps for the sudden perturbation, and simply requires to account for the additional factors $e^{\pm i\omega\tau}$ in the integrand of (19.26). The transition probability then has two maxima: one around $E_m = E_n - \hbar\omega$, associated with (stimulated) *emission* of an amount of energy $\hbar\omega$, and another around $E_m = E_n + \hbar\omega$, associated with *absorption* of an amount of energy $\hbar\omega$. The associated transition rates are given by

$$\Gamma_n = \frac{2\pi}{\hbar}|\hat{W}_{mn}|^2\rho(E_m) \quad \text{(emission, } E_m = E_n - \hbar\omega\text{)}, \quad (19.31)$$

$$\Gamma_n = \frac{2\pi}{\hbar}|\hat{W}_{mn}^\dagger|^2\rho(E_m) \quad \text{(absorption, } E_m = E_n + \hbar\omega\text{)}. \quad (19.32)$$

### E. Radiative transitions

An important application of Fermi's golden rule are transitions between two atomic energy levels $E_1$ and $E_2$, induced by the action of an (approximately) monochromatic electromagnetic field with central frequency tuned to $\omega = |E_2 - E_1|/\hbar$. Since the wavelength of the field is generally far larger than the extent of the atomic electronic orbitals, one can apply the *dipole approximation* in which the interaction is of the form

$$\hat{w}(t) = \hat{\boldsymbol{\mu}}\cdot\mathbf{E_0}(e^{i\omega t} + e^{-i\omega t}), \quad (19.33)$$

where $\hat{\boldsymbol{\mu}} = e\mathbf{r}$ is the *dipole operator*. Averaged over the direction of $\mathbf{E_0}$, the matrix element of the perturbation takes the form

$$|\hat{W}_{21}|^2 = \frac{|E_0|^2}{3}|\boldsymbol{\mu}_{21}|^2, \quad (19.34)$$

where

$$\boldsymbol{\mu}_{21} = e\iiint d^3\mathbf{r}\,\psi_2^*(\mathbf{r})\mathbf{r}\psi_1(\mathbf{r}) \quad (19.35)$$

is the matrix element of the dipole operator, evaluated with the two atomic wave functions involved in the transition (note that $\boldsymbol{\mu}_{21}$ is a three-component vector). Fermi's golden rule (19.31) gives

$$\Gamma_{1\to 2} = \frac{\pi|\boldsymbol{\mu}_{21}|^2}{3\varepsilon_0\hbar^2}\frac{I(\omega)}{c}, \quad (19.36)$$

where $I(\omega) = 2c\varepsilon_0|E_0|^2$ is the EM field intensity distribution. The corresponding energy density is $u = I/c$. The ratio $B_{1\to 2} = \Gamma_{1\to 2}/u(\omega)$, known as the *Einstein B coefficient*, is therefore approximated as

$$B_{1\to 2} = \frac{\pi|\boldsymbol{\mu}_{21}|^2}{3\varepsilon_0\hbar^2}. \quad (19.37)$$

For a pair of non-degenerate levels as considered so far, the coefficients for absorption and emission are identical. In the case of degeneracy, they differ by a factor $B_{1\to 2}/B_{2\to 1} = g_2/g_1$, which enters through the density of final states.

The above considerations apply to classical radiation. When the EM field is quantised, its energy is carried by photons whose number can fluctuate according to the probabilistic principles of quantum mechanics. These fluctuations give rise to *spontaneous emissions*. Avoiding details of the field quantisation, we obtain the rate for this processes by a phenomenological generalisation of Eq. (19.36). For this, we assume that the field fluctuations amount to an energy $\hbar\omega$ per electromagnetic mode. Combined with the local density of photon states per unit energy interval $\nu(\hbar\omega) = \omega^2/\pi^2\hbar c^3$

(see Eq. (13.21)), these fluctuations correspond to a classical field intensity of $I(\omega) = \hbar\omega^3/\pi^2\hbar c^2$. According to Eq. (19.36), the spontaneous emission rate for an atomic transition between two levels with energy difference $E_2 - E_1 = \hbar\omega$ (also known as the *Einstein A coefficient*) is, thus, given by

$$\Gamma_{1\to2}^{(sp)} = \frac{\omega^3}{3\pi\varepsilon_0\hbar c^3}|\boldsymbol{\mu}_{21}|^2. \qquad (19.38)$$

This expression typically allows to obtain highly accurate values for the life time of an electron in an atomic orbital. For example, for the transition $2p \to 1s$ in the hydrogen atom, the squared dipole matrix element is

$$|\boldsymbol{\mu}_{21}|^2 = \frac{2^{15}}{3^{10}}\left(\frac{4\pi\varepsilon_0\hbar^2}{\mu e}\right)^2 = (6.32 \times 10^{-30}\,\mathrm{C\,m})^2, \qquad (19.39)$$

where $\mu \approx m_e$ is the reduced mass of the electron. According to Eq. (19.38), with $\omega = (3/4)\,\mathrm{Ry}/\hbar = 1.55 \times 10^{16}\mathrm{s}^{-1}$, this amounts to a spontaneous emission rate $\Gamma = 6.27 \times 10^8\mathrm{s}^{-1}$. Perturbation theory is well justified because the rate $\Gamma \approx 4 \times 10^{-8}\,\omega$ is much smaller than the frequency $\omega$ of the emitted radiation. The associated decay time is $\tau = 1/\Gamma = 1.60 \times 10^{-9}\mathrm{s}$. We know from the discussion of the energy-time uncertainty principle that this decay results in a Lorentzian broadening of the emitted frequency intensity, with full width at half maximum $\Delta\omega = \Gamma$.

## XX. DIRAC NOTATION FOR COMPOSITE SYSTEMS

In preparation for the concluding chapter of this course, we now extend in this the Dirac notation to systems with more than one particle or several degrees of freedom, and also introduce a generalised notion of a state (the density matrix).

### A. Many degrees of freedom

Simultaneous observables appear in particular when a particle has many degrees of freedom, which may be continuous (like the three components of the position vector $\mathbf{r}$, discrete (like spin), or both (as for a single electron, which possess all these degrees freedoms). In ordinary notation, the state of the electron is described by a position-dependent spinor wavefunction

$$\psi = \begin{pmatrix} \psi^\uparrow(\mathbf{r}) \\ \psi^\downarrow(\mathbf{r}) \end{pmatrix}, \qquad (20.1)$$

where $|\psi^\uparrow(\mathbf{r})|^2$ is the probability density to find the electron at position $\mathbf{r}$ with spin $S_z = \hbar/2$ (spin up),

while $|\psi^\downarrow(\mathbf{r})|^2$ is the probability density to find the electron at position $\mathbf{r}$ with spin $S_z = -\hbar/2$ (spin down).

In Dirac notation, we can write these states in terms of a basis $|\mathbf{r}, S_z\rangle$, such that

$$|\psi\rangle = \int d\mathbf{r}\,\psi^\uparrow(\mathbf{r})|\mathbf{r}, \hbar/2\rangle + \int d\mathbf{r}\,\psi^\downarrow(\mathbf{r})|\mathbf{r}, -\hbar/2\rangle. \quad (20.2)$$

#### 1. Factorisation and entanglement

For the special case

$$|\psi\rangle = \int d\mathbf{r}\,\psi(\mathbf{r})(\psi^\uparrow|\mathbf{r}, \hbar/2\rangle + \psi^\downarrow|\mathbf{r}, -\hbar/2\rangle), \qquad (20.3)$$

where the amplitudes $\psi^\uparrow$ and $\psi^\downarrow$ do not depend on position, one says that the spinor wavefunction *factorises* into the orbital wavefunction $\psi(\mathbf{r})$ and the spinor $\begin{pmatrix} \psi^\uparrow \\ \psi^\downarrow \end{pmatrix}$. In the case that the wavefunction does not factorise one says that the spin and the position of the electron are *entangled*.

As a matter of fact, we encountered entanglement already in the context of the Stern Gerlach experiment. Ignoring the individual degrees of freedom, we can describe a silver atom by a spinor wavefunction (20.1), where $\mathbf{r}$ is the centre of mass of the atom and the spin is the total spin of the atom (in its ground state, the total spin of a silver atom is $\hbar/2$, just as for a single electron). In a Stern-Gerlach experiment, the wavefunction factorises before an atom enters the apparatus, since the path on which the atoms move from the oven towards the apparatus is independent of their spin state. Behind the apparatus, however, spin and position of the atoms have become entangled: The position at which an atom is collected on the screen depends on its spin (two spots are observed, where one corresponds to atoms with $S_z = \hbar/2$ and the other corresponds to $S_z = -\hbar/2$). This entanglement is created inside the apparatus, through the spin- and position-dependent interaction with the magnetic field.

### B. Density matrix

An *ensemble* is a large collection of physically identical quantum systems, which however can be described by different states. When all the states are identical the ensemble is said to be *pure*, otherwise it is *mixed*. In general, we specify that a fraction $P_i$ of states is in state $|\psi_i\rangle$, where $\sum_i P_i = 1$ and $\langle\psi_i|\psi_i\rangle = 1$. Starting from a pure ensemble with all members in state $|\psi\rangle$, such a mixed ensemble is obtained, e.g., by measurement of an observable,

with $P_i$ and $|\psi_i\rangle$ obtained as described in the previous section. In the ensemble, expectation values are defined by $\langle A \rangle = \sum_i P_i \langle \psi_i | \hat{A} | \psi_i \rangle$.

By construction, a mixed ensemble cannot be described by a single quantum state. However, it is possible to define a *statistical operator* $\hat{\rho}$, most commonly known as the *density matrix*, which allows to calculate all expectation values in a given mixed ensemble. This operator is given by

$$\hat{\rho} = \sum_i P_i |\psi_i\rangle\langle\psi_i|, \tag{20.4}$$

and the expectation values are obtained by

$$\langle A \rangle_\rho = \mathrm{tr}\,(\hat{A}\hat{\rho}). \tag{20.5}$$

Here, $\mathrm{tr}\,\hat{B}$ denotes the *trace* of an operator, which in any given orthonormal basis can be calculated as $\mathrm{tr}\,\hat{B} = \sum_n \langle n|\hat{B}n\rangle = \sum_n B_{nn}$.

Normalisation of states carries over to the property $\mathrm{tr}\,\hat{\rho} = 1$. Moreover, the density matrix is hermitian and positive definite. This entails that in its eigenrepresentation $\hat{\rho} = \sum_n p_n |n\rangle\langle n|$, all eigenvalues are nonnegative, $p_n > 0$; they also sum up to unity, $\sum_n p_n = 1$. (The nonvanishing eigenvalues $p_n$ are only identical to the values $P_i$ if the states $|\psi_i\rangle$ used to define the ensemble are orthogonal to each other.)

For a pure ensemble, $p_n = 1$ for one state, while all the other $p_m = 0$ ($m \neq n$). In this case, $\hat{\rho} = |n\rangle\langle n| = \hat{E}_n$ is a projection operator, and therefore fulfills $\hat{\rho}^2 = \hat{\rho}$. It follows that for a pure state $\mathrm{tr}\,\hat{\rho}^2 = 1$. For a mixed state, however $\mathrm{tr}\,\hat{\rho}^2 = \sum_n p_n^2 < 1$. The quantity $\mathcal{P} = \mathrm{tr}\,\hat{\rho}^2$, also known as the *purity*, therefore easily distinguishes pure from mixed states. The maximally mixed state is described by the density matrix $\hat{\rho} = \frac{1}{\mathcal{N}}\hat{I}$ (where $\mathcal{N}$ is the Hilbert space dimension), and has purity $\mathcal{P} = 1/\mathcal{N}$.

In a given representation, the density matrix of a pure state $|\psi\rangle$ can be obtained from $\rho = \psi\psi^\dagger$, which is useful for specific calculations.

The time evolution of the density matrix follows from the Schrödinger equation, and is given by $\frac{d}{dt}\hat{\rho} = \frac{i}{\hbar}[\hat{\rho}, \hat{H}]$. The general solution can be written as $\hat{\rho}(t) = \hat{U}(t, t_0)\hat{\rho}(t_0)\hat{U}^\dagger(t, t_0)$, where $\hat{U}$ is the unitary time evolution operator.

## C. Example: Two-state systems

Nature provides us with a wealth of quantum systems for which only two states are important. Besides spin, further examples are atomic transitions between the ground state and a selected excited state, the tunnelling of a particle between the almost-degenerate lowest-energy states of a double well, or two the orthogonal linear polarisation states of a photons. The quantum system can then be described by a spinor wavefunction $\binom{\alpha}{\beta}$, where the amplitudes $\alpha$ and $\beta$ are now associated, e.g., with the occupation probability of the ground or excited state in the atom, or describe whether the particle is located in the right or left trough of the double well.

In the Dirac notation, given an orthonormal basis $|0\rangle$, $|1\rangle$ the state of the system can be written as

$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle, \tag{20.6}$$

while the density matrix is of the general form

$$\hat{\rho} = \rho_{00}|0\rangle\langle 0| + \rho_{01}|0\rangle\langle 1| + \rho_{10}|1\rangle\langle 0| + \rho_{11}|1\rangle\langle 1|. \tag{20.7}$$

It is again useful to characterize the state (be it mixed or pure) by the polarisation vector

$$\vec{P} = (\langle X \rangle, \langle Y \rangle, \langle Z \rangle). \tag{20.8}$$

For a normalised pure state,

$$\vec{P} = (2\,\mathrm{Re}\,\alpha^*\beta, 2\,\mathrm{Im}\,\alpha^*\beta, |\alpha|^2 - |\beta|^2) \tag{20.9}$$

is of unit length, and therefore lies on the surface of the Bloch sphere. In terms of spherical polar coordinates on this sphere,

$$|\psi\rangle = \cos(\theta/2)|0\rangle + e^{i\phi}\sin(\theta/2)|1\rangle. \tag{20.10}$$

For a mixed state, $|\vec{P}| < 1$ so that the vector lies within the sphere. In terms of these expectation values, the components of the density matrix can be written as

$$\rho = \frac{1}{2}\begin{pmatrix} 1 + P_z & P_x - iP_y \\ P_x + iP_y & 1 - P_z \end{pmatrix} = \frac{1}{2}(I + P_x X + P_y Y + P_z Z). \tag{20.11}$$

The purity of this density matrix is given by $\mathcal{P} = \frac{1}{2}(1 + |\vec{P}|^2)$.

## D. Composite systems

Another important example where simultaneous observables occur are composite systems (say, a system composed of distinguishable parts 1 and 2), where incomplete information can be acquired by measuring an observable of a subsystem (say, part 1). Starting from an orthonormal basis $|n\rangle$ ($n = 1, \ldots, \mathcal{N}_1$) for system 1 and $|m\rangle$ ($m = 1, \ldots, \mathcal{N}_2$) for system 2, the joint state $|\psi\rangle = \sum_{nm} \psi_{nm}|nm\rangle$ of the composite system can be written by using combined basis states $|nm\rangle$, sometimes also written as $|n\rangle|m\rangle$ or $|n\rangle \otimes |m\rangle$. The corresponding dual basis

vectors are denoted by $\langle nm|$. The Hilbert space dimension of the composite system is therefore given by $\mathcal{N} = \mathcal{N}_1 \mathcal{N}_2$. General operators can be written as $\hat{A} = \sum_{nmkl} A_{nk,ml}|nk\rangle\langle ml|$. Operators acting on subsystem 1 will be denoted by $\hat{A}_1$, and have representation $\hat{A}_1 = \sum_{nmk} A_{nm}^{(1)}|nk\rangle\langle mk|$. Operators acting on subsystem 2 will be denoted by $\hat{A}_2$, and have representation $\hat{A}_2 = \sum_{nkl} A_{kl}^{(2)}|nk\rangle\langle nl|$. This results in the convenient *block matrix* form

$$A_1 = \begin{pmatrix} A_{11}^{(1)}I & A_{12}^{(1)}I & \cdots \\ A_{21}^{(1)}I & A_{22}^{(1)}I & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}, \quad A_2 = \begin{pmatrix} A^{(2)} & 0 & \cdots \\ 0 & A^{(2)} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix},$$
(20.12)

where $I$ is the $\mathcal{N}_2 \times \mathcal{N}_2$-dimensional identity matrix. Here, the basis states are ordered as $|1,1\rangle, |1,2\rangle, \ldots, |1,\mathcal{N}_2\rangle, |2,1\rangle, |2,2\rangle, \ldots$.

## E. Entanglement in composite systems

Sometimes, the state of a composite system can still be written as the product $|\varphi\rangle|\chi\rangle$ of two states, where $|\varphi\rangle$ describes system 1 and $|\chi\rangle$ describes system 2. Such states are called *separable*. This requires that the coefficients can be written as $\psi_{nm} = \varphi_n \chi_m$. States that are not separable are called *entangled*.

### 1. Reduced density matrix

In order to determine whether states are separable or entangled, it is useful to consider measurements of observables of one subsystem, say system 1. When a state is separable, $|\psi\rangle = |\varphi\rangle|\chi\rangle$, the outcome of such measurements only depends on $|\varphi\rangle$. However, when the system is entangled, measurements on one subsystem cannot be described by a single state of that system. It is then still possible to describe these measurements by a density matrix

$$\hat{\rho}_1 = \sum_{nmk} \langle nk|\psi\rangle\langle\psi|mk\rangle|n\rangle\langle m|, \tag{20.13}$$

known as the *reduced density matrix*. This means that all expectation values can be computed according to $\langle A\rangle = \operatorname{tr}\hat{A}\hat{\rho}_1$. Analogously, measurements of the second subsystem are described by a reduced density matrix $\hat{\rho}_2 = \sum_{nkl}\langle nk|\psi\rangle\langle\psi|nl\rangle|k\rangle\langle l|$. If a state $|\psi\rangle$ is separable, the reduced density matrices are pure, i.e., $\operatorname{tr}\hat{\rho}_1^2 = \operatorname{tr}\hat{\rho}_2^2 = 1$. If the state $|\psi\rangle$ is entangled, the reduced density matrices are both mixed, i.e., $\operatorname{tr}\hat{\rho}_1^2 = \operatorname{tr}\hat{\rho}_2^2 < 1$.

Reduced density matrices can also be defined when the composite system is already in a mixed state, described by a density matrix $\hat{\rho}$. They are then given by

$$\hat{\rho}_1 = \sum_{nmk}\langle nk|\hat{\rho}|mk\rangle|n\rangle\langle m|, \quad \rho_2 = \sum_{nkl}\langle nk|\hat{\rho}|nl\rangle|k\rangle\langle l|.$$
(20.14)

These constructions are also called *partial trace*, and then written as $\hat{\rho}_1 = \operatorname{tr}_2\hat{\rho}$, $\hat{\rho}_2 = \operatorname{tr}_1\hat{\rho}$. This designation becomes clear when one considers the block form

$$\rho = \begin{pmatrix} \rho_{11}^{(2)} & \rho_{12}^{(2)} & \cdots \\ \rho_{21}^{(2)} & \rho_{22}^{(2)} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \tag{20.15}$$

of the density matrix in the composite basis, where $\rho_{nm}^{(2)}$ are $\mathcal{N}_2 \times \mathcal{N}_2$-dimensional matrices. Then,

$$\rho_1 = \begin{pmatrix} \operatorname{tr}\rho_{11}^{(2)} & \operatorname{tr}\rho_{12}^{(2)} & \cdots \\ \operatorname{tr}\rho_{21}^{(2)} & \operatorname{tr}\rho_{22}^{(2)} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}, \quad \rho_2 = \sum_n \rho_{nn}^{(2)}. \tag{20.16}$$

In this more general case of a composite system with a mixed density matrix, the purities of both reduced density matrices do not need to be identical, and cannot simply be used to decide whether the system is entangled or not; this is discussed in more detail below.

### 2. Bell pairs and entanglement

As an example of a composite system, consider two two-state systems. Pure states can be written as $|\psi\rangle = \alpha|00\rangle + \beta|01\rangle + \gamma|10\rangle + \delta|11\rangle$, and are normalised if $|\alpha|^2 + |\beta|^2 + |\gamma|^2 + |\delta|^2 = 1$. An particularly interesting state is given by

$$|\psi\rangle = \frac{1}{\sqrt{2}}|01\rangle + \frac{1}{\sqrt{2}}|10\rangle. \tag{20.17}$$

This state is entangled: if the state of the first part of the system is determined through a measurement, one knows that the other part is in the opposite state, even though one has not carried out a measurement on this part.

In the general case, the entanglement of a state $|\psi\rangle$ is often characterised by the *concurrence*

$$\mathcal{C} = 2|\alpha\delta - \beta\gamma|, \tag{20.18}$$

which fulfills $0 \leq \mathcal{C} \leq 1$. For separable states, $\mathcal{C} = 0$, i.e., the concurrences vanishes. For entangled states, $\mathcal{C} > 0$. States with $\mathcal{C} = 1$ are called

maximally entangled. Examples of maximally entangled states are the four *Bell states*

$$|\beta_{00}\rangle = \sqrt{\frac{1}{2}}(|00\rangle + |11\rangle), \tag{20.19}$$

$$|\beta_{01}\rangle = \sqrt{\frac{1}{2}}(|01\rangle + |10\rangle), \tag{20.20}$$

$$|\beta_{10}\rangle = \sqrt{\frac{1}{2}}(|00\rangle - |11\rangle), \tag{20.21}$$

$$|\beta_{11}\rangle = \sqrt{\frac{1}{2}}(|01\rangle - |10\rangle). \tag{20.22}$$

For the pure state given above, the full density matrix

$$\rho = \begin{pmatrix} \alpha \\ \beta \\ \gamma \\ \delta \end{pmatrix} (\alpha^*, \beta^*, \gamma^*, \delta^*) = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \tag{20.23}$$

can be conveniently written in block form, where $A$, $B$, $C$, and $D$ are $2 \times 2$-dimensional matrices. The reduced density matrix

$$\rho_1 = \begin{pmatrix} \operatorname{tr} A & \operatorname{tr} B \\ \operatorname{tr} C & \operatorname{tr} D \end{pmatrix} \tag{20.24}$$

can then be obtained by taking traces of the blocks, which here results in

$$\rho_1 = \begin{pmatrix} |\alpha|^2 + |\beta|^2 & \alpha\gamma^* + \beta\delta^* \\ \gamma\alpha^* + \delta\beta^* & |\gamma|^2 + |\delta|^2 \end{pmatrix}. \tag{20.25}$$

Similarly,

$$\rho_2 = A + D = \begin{pmatrix} |\alpha|^2 + |\gamma|^2 & \alpha\beta^* + \gamma\delta^* \\ \beta\alpha^* + \delta\gamma^* & |\beta|^2 + |\delta|^2 \end{pmatrix}. \tag{20.26}$$

The purity of these reduced density matrices is related to the concurrence,

$$\operatorname{tr} \hat{\rho}_1^2 = \operatorname{tr} \hat{\rho}_2^2 = 1 - \mathcal{C}^2/2. \tag{20.27}$$

Furthermore, we have the identity $\det \hat{\rho}_1 = \mathcal{C}^2/4$.

For composite systems in a pure state, the reduced density matrix also delivers the *entanglement of formation* $\mathcal{E} = -\operatorname{tr}(\hat{\rho}_1 \log_2 \hat{\rho}_1) = -\operatorname{tr}(\hat{\rho}_2 \log_2 \hat{\rho}_2)$.

In their form discussed above, these measures of entanglement only apply to *pure* states of a composite system. Entanglement measures for multi-component systems with a mixed density matrix are an active field of research. Well understood is only the case of *two composite two-level systems*, for which entanglement measures can be computed efficiently from the $4 \times 4$ dimensional density matrix $\rho$ of the composite system in the standard basis. In order to obtain the concurrence, one needs to compute the four eigenvalues $\lambda_i$ of the matrix $\rho(Y_1 Y_2)\rho^*(Y_1 Y_2)$, where $Y_1$ and $Y_2$ are the $Y$ Pauli matrix acting on subsystem 1 and 2, respectively. When the eigenvalues are ordered such that $\lambda_1 > \lambda_2 > \lambda_3 > \lambda_4$, the concurrence is given as $\mathcal{C} = \max(0, \sqrt{\lambda_1} - \sqrt{\lambda_2} - \sqrt{\lambda_3} - \sqrt{\lambda_4})$. The entanglement of formation $\mathcal{E} = \min_{\text{dec}} \sum_i P_i \mathcal{E}(\psi_i)$ is generalised by minimizing the averaged pure-state entanglement of formation over all possible decompositions $\hat{\rho} = \sum_i P_i |\psi_i\rangle\langle\psi_i|$ of the density matrix (where the states $|\psi_i\rangle$ do not need to be orthogonal). Remarkably, both entanglement measures are related by the general formula $\mathcal{E} = h(\frac{1}{2} + \frac{1}{2}\sqrt{1 - \mathcal{C}^2})$, where $h(x) = -x \log_2 x - (1-x) \log_2(1-x)$.

### 3. Einstein, Podolsky, and Rosen

Here are some interesting thoughts about Bell pairs, raised by Einstein, Podolsky, and Rosen at a time (1935) when quantum mechanics was not yet totally accepted: When one measures a part of a system in a Bell pair, one gets a random result $0$ or $1$ with probability $1/2$. However, when one determined the state of part one of the system and communicated the result to the location of part 2, one would be able to predict the outcome of the measurement of the second part with certainty. This influence of the one experiment on the other was termed the 'ghostly action at a distance'.

Maybe the randomness of quantum mechanics is always of this kind, namely encoded in other degrees of freedom (so-called hidden variables) and all randomness would disappear when one would account for the state of these hidden variables? In 1965, John Bell showed that quantum mechanics predicts correlations between the two two-state systems which cannot be explained by a local hidden variable theory (we discuss the details of these considerations below). In the early 1980's, the existence of these correlations have been tested and confirmed by Alain Aspect and co-workers for the polarisation states of entangled photons.

These experiments are considered to be a proof of Bell's theorem: *No physical theory of local hidden variables can ever reproduce all of the predictions of quantum mechanics.* Hence, the uncertainties and randomness in the outcome of experiments in quantum mechanics are fundamentally different than mere statistical uncertainties in classical theories (e.g., in classical thermodynamics the statistical uncertainties arise from the uncontrolled microsocopic motion of the particles, which may still be deterministic, i.e., based on Newton's laws of motion).

### 4. Bell inequalities

Entanglement is physically significant because it results in correlations that cannot be described by classical probabilities. These correlations can be uncovered by statistical tests, known as *Bell inequalities*. The most transparent inequality is the *CHSH inequality* due to Clauser, Horn, Shimony, and Holt. Consider the composition of two two-state systems; to be explicit, think of the spins of two electrons with basis states $|0\rangle = |\uparrow\rangle$ and $|1\rangle = |\downarrow\rangle$. On each spin we carry out two different experiments, described by observables $\hat{A}_1$, $\hat{A}_1'$, $\hat{B}_2$, and $\hat{B}_2'$, which measure whether the spin points into a particular direction. To the outcome of each experiment we designate the value $1$ or $-1$, depending on whether the spin is found to be aligned parallel or antiparallel to the measurement direction, respectively. Now consider the expectation value of

$$\hat{F} = (\hat{A}_1 + \hat{A}_1')\hat{B}_2 - (\hat{A}_1 - \hat{A}_1')\hat{B}_2'. \qquad (20.28)$$

Classically, for each combination of outcomes, $F$ is either $2$ or $-2$, and therefore on average $\langle F \rangle \leq 2$, which is the CHSH inequality. Quantum-mechanically, the average is obtained by an expectation value. Let us choose $\hat{A}_1 = Z$, $\hat{A}_1' = X$, $\hat{B}_2 = -\sqrt{1/2}(X + Z)$, and $\hat{B}_2' = \sqrt{1/2}(X - Z)$, so that $\hat{F} = -\sqrt{2}(X_1 X_2 + Z_1 Z_2)$, which is represented by the matrix

$$F = -\sqrt{2} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & -1 & 1 & 0 \\ 0 & 1 & -1 & 0 \\ 1 & 0 & 0 & 1 \end{pmatrix}. \qquad (20.29)$$

Furthermore, assume that the system is in the Bell state $|\beta_{11}\rangle = \sqrt{1/2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$, represented by the vector

$$\psi = \sqrt{1/2} \begin{pmatrix} 0 \\ 1 \\ -1 \\ 0 \end{pmatrix}. \qquad (20.30)$$

We then find $\langle \hat{F} \rangle = \psi^\dagger F \psi = 2\sqrt{2}$, which violates the CHSH inequality. The reason are quantum-mechanical correlations that arise as a consequence of the entanglement of the Bell state. Quantum computation taps into this resource to achieve tasks that are classically impossible.

## XXI. MANY PARTICLES

Quantum mechanics takes one more twist when we consider a system containing many *indistinguishable* particles. By this we many particles that share the same physical characteristics like mass, charge, overall spin, etc; examples are collections of many electrons, or even collections of many identical atoms (which themselves are composite systems).

Assume, therefore, that there are several quantum particles, labelled $1, 2, 3, \ldots$, which can be found at positions $\mathbf{r_1}$, $\mathbf{r_2}$, $\mathbf{r_3}$, .... Some of the particles may also have spin $s_1$, $s_2$, $s_3$, .... The spin can take values $s_i = m\hbar$ where $m = -S_i, -S_i + 1, \ldots, S_i$. Particles are called bosons when $S_i$ is an integer (an example is the photon, with $S = 1$). Particles are called fermions when $S_i$ is a halfinteger (i.e., an integer plus $1/2$). Examples are electrons and protons, which have $S = 1/2$.

### A. Distinguishable particles

For a collection of distinguishable particles, we can follow the description of systems with many degrees of freedom. The total wavefunction is given by $\psi(\mathbf{r_1}, s_1, \mathbf{r_2}, s_2, \mathbf{r_3}, s_3, \ldots)$. An example is the wave function $\psi(\mathbf{r_p}, s_p, \mathbf{r_e}, s_e)$ describing the proton and the electron in a hydrogen atom.

### B. Indistinguishable particles

For indistinguishable particles, the total wavefunction is still a function $\psi(\mathbf{r_1}, s_1, \mathbf{r_2}, s_2, \mathbf{r_3}, s_3, \ldots)$, but probabilities cannot depend on the order of the labels:

$$|\psi(\mathbf{r_1}, s_1, \mathbf{r_2}, s_2, \mathbf{r_3}, s_3 \ldots)|^2 = |\psi(\mathbf{r_2}, s_2, \mathbf{r_1}, s_1, \mathbf{r_3}, s_3, \ldots)|^2, \qquad (21.1)$$

and similarly for the interchange of the other labels. This leaves two options. The first option is

$$\psi(\mathbf{r_1}, s_1, \mathbf{r_2}, s_2, \mathbf{r_3}, s_3 \ldots) = \psi(\mathbf{r_2}, s_2, \mathbf{r_1}, s_1, \mathbf{r_3}, s_3, \ldots), \qquad (21.2)$$

etc: The wavefunction is *symmetric*. This case is found when the particles are bosons. The second option is

$$\psi(\mathbf{r_1}, s_1, \mathbf{r_2}, s_2, \mathbf{r_3}, s_3 \ldots) = -\psi(\mathbf{r_2}, s_2, \mathbf{r_1}, s_1, \mathbf{r_3}, s_3, \ldots), \qquad (21.3)$$

etc: The wavefunction is *antisymmetric*. This case is found when the particles are fermions.

### C. Pauli exclusion principle

In the case of fermions, Eq. (21.3) implies that the probability to find two particles at the same point in space is zero if their spin state is the same:

$$\psi(\mathbf{r_1}, s_1, \mathbf{r_1}, s_1, \mathbf{r_3}, s_3 \ldots) = -\psi(\mathbf{r_1}, s_1, \mathbf{r_1}, s_1, \mathbf{r_3}, s_3, \ldots), \qquad (21.4)$$

hence

$$\psi(\mathbf{r_1}, s_1, \mathbf{r_1}, s_1, \mathbf{r_3}, s_3 \ldots) = 0. \qquad (21.5)$$

This is called the *Pauli exclusion principle*, which has numerous important consequence ranging from the allowed configurations of occupied orbitals by electrons in an atom and the periodic table of elements (both discussed below) over the general structure of matter to the properties of neutron stars.

## D. Two-electron orbitals

The wavefunction of two electrons can be grouped into a vector

$$\psi = \begin{pmatrix} \psi(\mathbf{r_1}, \uparrow, \mathbf{r_2}, \uparrow) \\ \psi(\mathbf{r_1}, \downarrow, \mathbf{r_2}, \uparrow) \\ \psi(\mathbf{r_1}, \uparrow, \mathbf{r_2}, \downarrow) \\ \psi(\mathbf{r_1}, \downarrow, \mathbf{r_2}, \downarrow) \end{pmatrix}. \qquad (21.6)$$

Typical two-electron wavefunctions which satisfy Eq. (21.3) are of the form

$$[\psi_1(\mathbf{r_1})\psi_2(\mathbf{r_2}) - \psi_1(\mathbf{r_2})\psi_2(\mathbf{r_1})] \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \qquad (21.7)$$

$$[\psi_1(\mathbf{r_1})\psi_2(\mathbf{r_2}) - \psi_1(\mathbf{r_2})\psi_2(\mathbf{r_1})] \begin{pmatrix} 0 \\ 1/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \end{pmatrix}, \qquad (21.8)$$

and

$$[\psi_1(\mathbf{r_1})\psi_2(\mathbf{r_2}) - \psi_1(\mathbf{r_2})\psi_2(\mathbf{r_1})] \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}. \qquad (21.9)$$

In all these cases the orbital part is antisymmetric and the spin part is symmetric. These states are called *triplet states* and correspond to a total spin of $\hbar$ (i.e. the spin of the two electrons is parallel and adds up). There is only a single state where the spin is anti-parallel:

$$[\psi_1(\mathbf{r_1})\psi_2(\mathbf{r_2}) + \psi_1(\mathbf{r_2})\psi_2(\mathbf{r_1})] \begin{pmatrix} 0 \\ 1/\sqrt{2} \\ -1/\sqrt{2} \\ 0 \end{pmatrix}. \qquad (21.10)$$

This state corresponds to a total spin of 0 and has a symmetric orbital part.

When the orbital wavefunctions are identical, $\psi_1 = \psi_2$, then the triplet states vanish. This is a consequence of the Pauli exclusion principle: Two electrons cannot have the same orbital wavefunction if their spin is parallel.

## E. Two electrons in a harmonic-oscillator potential

Recall that the single-particle states in a harmonic-oscillator potential are enumerated by a quantum number $|n\rangle$, $n = 0, 1, \ldots,$, and associated with an energy $E_n = \hbar\omega(n + 1/2)$. If we load electrons into such a harmonic trap we also have account for the spin degree of freedom, thus resulting in states $|n, \uparrow\rangle$ and $|n, \downarrow\rangle$ whose energies are degenerate, $E_{n,\uparrow} = E_{n,\downarrow} = E_n$.

For two electrons, we now have to distinguish several situations:

If the spins are identical, e.g., pointing up, we then have to work in the basis of states $|n\uparrow; m\uparrow\rangle$. The spin part of this is symmetric, and thus the antisymmetry required by the Pauli principle must arise from the orbital part, giving rise to a structure

$$|n\uparrow; m\uparrow\rangle - |m\uparrow; n\uparrow\rangle = (|nm\rangle - |mn\rangle)|\uparrow\uparrow\rangle, \quad (21.11)$$

where we formally separated the orbital and spin parts of the state. In terms of wave functions, the orbital part is of the structure $\psi_n(x_1)\psi_m(x_2) - \psi_m(x_1)\psi_n(x_2)$, where $x_i$ are the coordinates of the two electrons. This state vanishes if $n = m$. In particular, the lowest-energy state of the system is $(|01\rangle - |10\rangle)|\uparrow\uparrow\rangle$; this has energy $E_{01} = E_0 + E_1 = 2\hbar\omega$.

If the spins are non-identical, we have to work in the basis of states $|n\uparrow; m\downarrow\rangle$ and $|n\downarrow; m\uparrow\rangle$. The spin part may still be symmetric, which is realised by states of the form

$$|n\uparrow; m\downarrow\rangle + |n\downarrow; m\uparrow\rangle - |m\uparrow; n\downarrow\rangle - |m\downarrow; n\uparrow\rangle$$
$$= (|nm\rangle - |mn\rangle)(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle). \qquad (21.12)$$

Again, these states vanish for $n = m$. This exhausts the triplet states, which are all constrained by the Pauli principle. However, the spin part may now also be antisymmetric, which is realised by states of the form

$$|n\uparrow; m\downarrow\rangle - |n\downarrow; m\uparrow\rangle + |m\uparrow; n\downarrow\rangle - |m\downarrow; n\uparrow\rangle$$
$$= (|nm\rangle + |mn\rangle)(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \qquad (21.13)$$

These are singlet states, for which $n$ and $m$ may be equal. This includes the lowest-energy state $|00\rangle(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$, which possesses energy $E_{00} = 2E_0 = \hbar\omega$.

## F. The periodic table of chemical elements

The periodic table of elements is composed of atoms with a nucleus of charge $Ze$, which attracts $Z$ electrons. A qualitative understanding can be obtained by ignoring the interaction between the electrons. Then the electronic states are given by

the states $\psi_{nml} = R_n Y_{lm}$ of the hydrogen atom, but with the charge $e$ of the nucleus replaced by $Ze$. The ground state of an atom is obtained by occupying these states starting with the lowest energy state $1s$, then $2s$ and $2p$, then $3s$, $3p$. (After this point interactions start to change the systematics slightly: The 4s orbital is filled before 3d.) Because of the Pauli principle, each state can accommodate only two electrons, which have to have opposite spin.

Examples: Helium (He) has $Z = 2$ (the nucleus consists of two protons and two neutrons). Hence, it has two electrons, which occupy the 1s orbital with opposite spin. The electronic charge density is spherical symmetric, and exciting an electron into the 2s or 2p orbital would cost a relatively large amount of energy. This explains why He is chemically inert.

Neon (Ne) has $Z = 10$, hence all states in 1s, 2s and 2p are occupied. Again, the charge distribution is spherical symmetric and the excitation energy to the 3s, 3p and 3d orbitals prevents this atom from being chemically active. Atoms of similar properties as He or Ne (noble gases) are all found in the last column of the periodic table.

Sodium (Na) has $Z = 11$. Ten electrons occupy the 1s, 2s, and 2p orbitals, like in Ne, and the extra eleventh electron occupies the 3s orbital. Its chemical properties are typical for the alkali metals, which are all found in the first column of the periodic table, and all have the electronic structure of a noble gas plus one extra electron in an s orbital. Alkali atoms like to bind to halogens, the atoms in the last-but-one column, which lack one electron for a spherically symmetric electronic configuration. When an alkali atom binds to a halogen atom, the alkali atom donates and electron to the halogen atom, which is energetically favorable; both atoms then are spherically symmetric and oppositely charged, and attract each other by the Coulomb force.

### G. Quantum statistical mechanics

We finally turn to a brief discussion of the consequences of quantum mechanics for *statistical mechanics*, which concerns the thermodynamical description of large composite systems in (or close) to equilibrium. This topic brings us right back to the historical origin of quantum mechanics: Max Planck's hypothesis that the energy of systems can be quantised. That we can discuss these consequences solidly only at the end of this course is testament to the depth of this original concept (and well justifies the appellation *quantum mechanics*

for the theory that emerged from it).

Thermodynamics enjoys a firm theoretical foundation relying on statistical considerations of the occupation probability of all possible microstates, as pioneered by Ludwig Boltzmann, who introduced statistical weights which relate the occupation probability to energy and temperature. Quantum mechanics fundamentally affects and shapes all aspects of this description via the concepts of energy quantisation, rules to calculate occupation probabilities, and the Pauli principle which implies restrictions for the states of indistinguishable particles, of which there are two variants, bosons and fermions.

### 1. Boltzmann distribution

The *Boltzmann distribution* assigns the value

$$P_n = \frac{1}{Z(T)} g_n \exp(-E_n/kT) \qquad (21.14)$$

to the probability that a thermodynamical system occupies a microstate of energy $E_n$ and degeneracy $g_n$, where $k$ is Boltzmann's constant, $T$ is temperature, and

$$Z(T) = \sum_n g_n \exp(-E_n/kT) \qquad (21.15)$$

is the *partition function* which ensures normalisation of the occupation probabilities.

Quantum mechanically, this corresponds to a density matrix

$$\hat{\rho} = \frac{1}{Z(T)} \exp(-\hat{H}/kT), \qquad (21.16)$$

where now normalisation enforces $Z(T) = \mathrm{tr}\,\hat{\rho}$.

### 2. Fermi-Dirac statistics

Consider a thermodynamical systems which is made out of identical components. Starting from the Boltzmann distribution of the combined system we can derive probability distributions for states individual components.

The simplest case concerns fermions, since here each single-particle state $|i\rangle$ can be occupied at most with probability one. In a measurement, this corresponds to only two choices: The state is occupied or empty. Based on the Boltzmann distribution for the microstates of the total system, the average number of fermions occupying this then follows the *Fermi-Dirac distribution*

$$\bar{n}_i = \frac{1}{\exp[(\varepsilon_i - \mu)/kT] + 1}, \qquad (21.17)$$

where $\mu$ is the *chemical potential*, which is independent of the index $i$ and can be determined by knowledge of the total number $N = \sum_i \bar{n}_i$ of particles in the system.

At low temperatures, the Fermi-Dirac distribution behaves like a unit step function, $\bar{n}_i \approx \Theta(E_F - \varepsilon_i)$, where $E_F$ is the *Fermi energy*. In many applications, the Fermi energy is very large. An important example are electrons in metals, which typically have a Fermi energy $E_F$ is many thousands of kelvins). Electrons in a metal can be treated as weakly interacting, and therefore are a good approximation of a (*Fermi gas*). For $E_F \ll T$ (i.e., at room temperature and below), the gas is called *degenerate*.

Further examples of degenerate Fermi gases are neutron stars (a degenerate gas of neutrons) and white dwarf stars (a degenerate gas of electrons). A degenerate gas is difficult to compress since the density of states decreases with volume, upon which the Pauli principle enforces occupation of highly energetic levels. This corresponds to a large *degeneracy pressure* which stabilizes white dwarfs and neutron stars against gravitational collapse as long as they are not too heavy. (White dwarfs are stable below the Chandrasekhar limit of about 1.4 solar masses; exceeding this limit they may explode in a Type Ia supernova. Neutron stars are formed as remnants of Type II, Type Ib or Type Ic supernovae, involving more massive stars. Above 3-4 solar masses, the degeneracy pressure of the neutrons is overcome by gravity, which may lead to the formation of a black hole.)

### 3. Bose-Einstein statistics

Bosons are not subject to the Pauli exclusion principle, so that each single-particle state can be occupied an arbitrary number of times. The Boltzmann distribution for the microstates of the total system then yields the *Bose-Einstein distribution*

$$\bar{n}_i = \frac{1}{\exp[(\varepsilon_i - \mu)/kT] - 1}, \qquad (21.18)$$

which differs from the Fermi-Dirac distribution only by a $-$ sign in the denominator.

At low temperatures, the chemical potential of a weakly interacting *Bose gas* tends to zero. Below a critical temperature, the ground state becomes populated by finite fraction of the total number of boson, and the gas forms a *Bose-Einstein condensate*, as first realised in 1995 by Eric Cornell, Carl Wieman, and co-workers with atomic gases at sub-micro Kelvin temperatures. Analogously,

more strongly interacting bosons may form a *superfluid* with zero viscosity, as first observed for Helium-4 (by Pyotr Kapitsa, John Allen and Don Misener, in 1938). Under some circumstances, strongly bound pairs of fermions can effectively behave like bosons. These can condense to form fermionic superfluids, like a superfluid of electronic *Cooper pairs* in a superconductor (as proposed by John Bardeen, Leon Cooper and Robert Schrieffer in 1957; superconductivity was discovered by Heike Kamerlingh Onnes in 1911), or a superfluid of Helium 3 (as confirmed by Douglas D. Osheroff, in 1971).

### 4. Maxwell-Boltzmann statistics

At large temperatures and low densities, the Fermi-Dirac distribution and the Bose-Einstein distribution tend to the same limit, the *Maxwell-Boltzmann distribution*

$$\bar{n}_i = \exp[-(\varepsilon_i - \mu)/kT]. \qquad (21.19)$$

For a gas, this approximation is valid if its particle concentration $c$ is much smaller than the *quantum concentration* $c_Q = (mkT/2\pi\hbar^2)^{3/2}$. This defines the limit of a *non-degenerate* gas.

### 5. Planck's law of black body radiation

As an application we consider the problem of electromagnetic radiation intensity emitted by a *black body*, an object that perfectly absorbs all incident electromagnetic radiation. Classical treatment of this radiation leads to two contradictory predictions, Wien's law (which is only accurate at high frequencies), and the Rayleigh-Jeans law (which is only accurate at low frequencies). This impasse led Planck to formulate his quantisation hypothesis. The problem is then solved by combining the density of electromagnetic field states

$$\rho(\omega) = L^3 \frac{\omega^2}{\pi^2 c^3} \qquad (21.20)$$

per unit angular frequency interval with the occupation probability

$$\bar{n}(\omega) = \frac{1}{\exp[\hbar\omega/kT] - 1} \qquad (21.21)$$

of photons with energy $\hbar\omega$. This delivers an energy density

$$u(\omega, T) = \frac{1}{L^3} \hbar\omega\rho(\omega)\bar{n}(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{\exp[\hbar\omega/kT] - 1}. \qquad (21.22)$$

The direction-resolved spectral intensity per unit solid angle is given by

$$I(\omega, T) = \frac{cu(\omega)}{4\pi} = \frac{\hbar\omega^3}{4\pi^3 c^2} \frac{1}{\exp[\hbar\omega/kT] - 1}. \quad (21.23)$$

In terms of the ordinary frequency $\nu = \omega/2\pi$, this delivers *Planck's law*

$$I(\nu, T) = 2\pi I(\omega = 2\pi\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{\exp[h\nu/kT] - 1}, \quad (21.24)$$

where we introduced (for good measure) Planck's original constant $h = 2\pi\hbar = 6.62606896(33) \times 10^{-34}\,\mathrm{J\,s}$.