

## TILLEGG 1

# 1. Introduction to quantum mechanics

Chapter 1 of the this course — Introduction to quantum mechanics — is covered by the present notes, “Tillegg 1”. In this chapter, we consider some of the milestones in the historical development of quantum mechanics. Chapter 1 in Bransden & Joachain gives a more comprehensive review and should be consulted for more details.

Quantum mechanics — to put it a bit too simply — is our theory of the submicroscopic world. This world is not so easily accessible for observations as macroscopic physics. This is why the discovery of most of the quantum phenomena, and their explanation, came as late as in the beginning of the last century.

At the beginning of the quantum era — in the year 1900 — classical physics appeared to be an almost complete physical theory:

- Newton’s mechanics had been established for more than two hundred years.
- The wave nature of light was known from the beginning of the 19th century, based on diffraction experiments carried out by Young and Fresnel, among others.
- The relation between electric and magnetic phenomena had been clarified, particularly through the work of Faraday and Maxwell, culminating with Maxwell’s equations in the 1860’s. Maxwell’s prediction of electromagnetic waves in 1865, and the experimental verification by Hertz in 1887, led to the understanding that also light is an electromagnetic wave phenomenon.
- In addition, thermodynamics and statistical mechanics were developed during the 19th century.

At the end of the century, these theories were by many people considered to give an almost complete description of the physical world. A few years later, it was clear that this was far from the truth:

- Newton’s laws turned out to be a limiting case (for small velocities) of Einstein’s special theory of relativity.
- Newton’s theory of gravitation was extended to (replaced by) Einstein’s general theory of relativity.
- The discovery that the atom consists of a very small and compact nucleus surrounded by pointlike electrons, and certain properties of the interaction between atoms and radiation, led to the development of the theory of quantum mechanics.

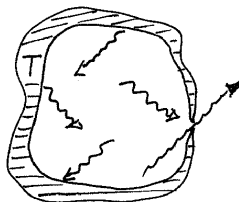
These theories and the development that followed later in the twentieth century have revolutionized our physical picture of the world, and have led to a number of advances in our understanding of atomic physics, nuclear physics, particle physics, astrophysics and cosmology, and also within chemistry, biophysics and biology and of course also within solid-state physics, including applications in technology.

Quantum mechanics contains a number of elements which are rather revolutionary compared to classical mechanics and our classical way of thinking. Therefore we may state that the “birth” of this theory was rather “painful” and took a long time, starting in 1900 and culminating in 1925, when there was a sudden breakthrough. After that, it took only a couple of years to obtain a fully developed theory. The reason for the difficult birth lies in the fact that this theory not only disagrees with classical physics, but also is **counter-intuitive**; it does not agree with the physical intuition which we develop based on our every-day experiences with macroscopic phenomena.

In what follows we shall review the main events in the development of quantum mechanics, and we shall see how the physics community gradually was forced to accept this revolutionary physical theory:

## 1.1 Planck’s radiation law (1900)

The discovery of the radiation law is discussed in section 1.1 in Bransden & Joachain. (See also 1.2 in Hemmer.) As explained there, a small opening to a cavity kept at a temperature  $T$  will radiate as a black-body surface at this temperature:



Planck found an empirical formula for the **spectral emittance** (emitted energy flux per unit area and unit frequency) from a black surface, based on experimental results that had just been obtained,

$$I(\nu, T) = \frac{2\pi\nu^2}{c^2} \frac{h\nu}{e^{h\nu/k_B T} - 1}. \quad (\text{T1.1})$$

At equilibrium, and supposing that also the inside walls of the cavity are black, there must be a relation between this spectral emittance from the walls and the **spectral energy density** inside the cavity,  $u(\nu, T)$ . It can be shown that  $I(\nu, T) = u(\nu, T) \cdot c/4$ , so that

$$u(\nu, T) = \frac{4}{c} I(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/k_B T} - 1}. \quad (\text{T1.2})$$

These two formulae are two equivalent ways of expressing Planck’s radiation law.

What was really remarkable with Planck’s empirical formula, was that it was a very good fit to the experimental frequency distribution of the radiation, not only for one particular

temperature; it did in fact fit to the distributions for a whole range of temperatures, and this was very strange, considering the fact that the formula contains *only one parameter*, beside the velocity of light  $c$ , Boltzmann's constant  $k_B$  and the temperature  $T$ . This was the parameter  $h$ , introduced by Planck. Planck understood that this meant that that the formula could be due to some underlying law, and immediately went to work trying to deduce the formula theoretically. After a couple of months he succeeded in deriving the formula using a certain physical model.

In this model, there is at equilibrium a constant exchange of energy between the radiation field inside the cavity and oscillating charges in the walls. According to Maxwell's theory, an oscillating charge can radiate energy as well as absorb it. To explain the continuous frequency distribution, Planck had to assume that the wall had "oscillators" with all kinds of frequencies. Furthermore he had to introduce into his model an assumption which was totally opposed to the principles of classical physics:

He had to assume that the energy of a given oscillator with frequency  $\nu$  was **quantized**, having the values  $nh\nu$ . Here  $\nu$  is the frequency,  $n$  is an integer and the proportionality constant  $h$  is the empirical parameter mentioned above. This assumption implies that the energy is exchanged in **quanta**  $h\nu$  between the radiation field and the oscillator.

By comparing with the experimental curves, Planck was able to determine his constant  $h$  to  $h \approx 6.6 \times 10^{-34}$  Js. Thus, Planck succeeded in deriving the radiation law, but he had to sacrifice a basic classical principle, introducing the **quantization** described above. Planck himself, being a truly "classical" physicist, described his quantization assumption as "an act of desperation".

**A small exercise:** Show that the total emittance  $I(T)$  (radiated energy per unit time and area) from a black surface at the temperature  $T$ ,

$$I(T) = \int_0^{\infty} I(\nu, T) d\nu,$$

is proportional to  $T^4$ , that is,  $I(T) = \sigma T^4$ , and determine the proportionality constant  $\sigma$  (which is called Stefan–Boltzmanns constant), given that

$$\int_0^{\infty} x^3 (e^x - 1)^{-1} dx = \pi^4/15.$$

[Hint: Use  $x = h\nu/k_B T$  as a new integration variable. Answer:  $\sigma = 5.670 \cdot 10^{-8}$  Wm<sup>-2</sup>K<sup>-4</sup>. See the table of physical constants at the end of this "Tillegg".]

## 1.2 Einstein explains the photoelectric effect (1905)

The photoelectric effect is described in section 1.3 (pp 12–13) in Hemmer, and in section 1.2 in Bransden & Joachain, which you should now read.

Compared to Plank's assumption mentioned above, Einstein took a new step which was for many years considered to be *too* radical: He assumed that the quantization had something to do with the *light itself*, implying that light and other electromagnetic radiation

consists of **discrete quanta** (light quanta, later christened **photons** by G.N. Lewis, in 1926) with energy  $h\nu$ . This proposal was met with large skepticism, which can be illustrated by the following citation from a proposal (in 1913) for Einstein's membership in the Prussian Academy of Sciences, signed by Planck and several other merited physicists: "In sum, it can be said that among the important problems, which are so abundant in modern physics, there is hardly one in which Einstein did not take a position in a remarkable manner. That he might sometimes have overshot the target in his speculations, as for example in his light quantum hypothesis, should not be counted against him too much. Because without taking a risk from time to time it is impossible, even in the most exact natural science, to introduce real innovations..."

This skepticism even lasted after the work by Millikan in the period 1914 – 16. Millikan obtained an accurate experimental verification of Einstein's equation for the kinetic energy of the emitted photo-electrons,

$$E_{\text{kin}} = h\nu - W,$$

and used his experimental data to obtain an independent determination of Planck's constant,

$$h = 6.57 \times 10^{-34} \text{ Js}.$$

This value deviates from the today's accurate value,

$$h = 6.626\,068\,96(33) \times 10^{-34} \text{ Js} \approx 4.136 \times 10^{-15} \text{ eVs},$$

by only 0.5 %. Millikan regarded this as a verification of Planck's hypothesis, as we can see from the following citation from one of his articles: "The photoelectric effect...furnishes proof which is quite independent of the facts of blackbody radiation of the correctness of the fundamental assumption of the quantum theory, namely, the assumption of a discontinuous or explosive emission of the energy absorbed by the electronic constituents of atoms from...waves. It materializes, so to speak, the quantity  $h$  discovered by Planck through the study of blackbody radiation and gives us a confidence inspired by no other type of phenomenon that the primary physical conception underlying Planck's work corresponds to reality."

But Einstein's idea was very difficult to accept. In Millikan's article from 1916 he states: "Einstein's photoelectric equation...cannot in my judgment be looked upon at present as resting upon any sort of a satisfactory theoretical foundation", even though "it actually represents very accurately the behavior" of the photoelectric effect.

Einstein, however, could not be stopped. After having completed his general theory of relativity, he extended his hypotheses on light quanta in 1917:

A light quantum with energy  $E = h\nu$  is assumed to have a momentum

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda}. \quad (\text{T1.3})$$

The background for this proposal is:

(i) Firstly, it follows from Maxwell's equations that an electromagnetic wave group (pulse) has a field energy  $E_{\text{field}}$  and a field momentum  $\mathbf{p}_{\text{field}}$  which satisfy the relation

$E_{\text{field}} = c|\mathbf{p}_{\text{field}}|$ . The fact that electromagnetic radiation also contains a momentum  $|\mathbf{p}| = E/c$  was verified experimentally by E.F. Nichols and G.F. Hull in 1903. If the electromagnetic pulse is to be regarded as a collection of light quanta (photons), then these quanta must also carry a momentum, in addition to the energy.

(ii) Secondly, it follows from relativistic particle kinematics,

$$E = \frac{mc^2}{\sqrt{1 - v^2/c^2}}, \quad p = \frac{mv}{\sqrt{1 - v^2/c^2}} \implies \frac{E}{p} = \frac{c^2}{v}, \quad E = \sqrt{m^2c^4 + c^2p^2}, \quad (\text{T1.4})$$

that  $E/p \rightarrow c$  when  $m \rightarrow 0$ .

The reason that these hypotheses were met with such a large skepticism was that they seemed to be in contradiction with all the knowledge that had been gained about the wave nature of light. How could light be both a wave and a stream of particles? The natural answer to this question was to discard Einstein's photon hypothesis, and this was the ruling opinion for several years after Millikan's work. This easy way out of the problem was finally blocked in 1923, through the discovery of the Compton effect.

**A small exercise:** From Einstein's photon hypothesis and Planck's radiation law (T1.2) it follows that the number of photons per unit volume and frequency in an oven at temperature  $T$  is  $n(\nu, T) = u(\nu, T)/h\nu$ . Show that the number of photons per unit volume,  $n(T) = \int_0^\infty n(\nu, T)d\nu$ , is

$$n(T) = 2.029 \cdot 10^7 \text{ T}^3 \text{ m}^{-3} \text{ K}^{-3},$$

and that the average energy of these photons is

$$\bar{E} = \frac{u(T)}{n(T)} = 2.701 k_B T,$$

given that  $\int_0^\infty x^2(e^x - 1)^{-1}dx = 2.4041$ .

**Another exercise:** Show that a photon with wavelength  $\lambda$  has the energy

$$E_\gamma = 1.24 \cdot 10^{-6} \frac{\text{eVm}}{\lambda}. \quad (\text{T1.5})$$

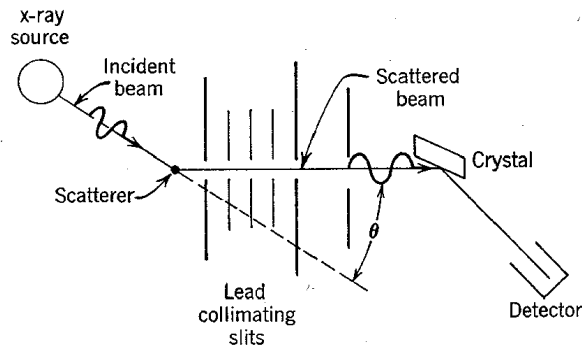
[Hint: At the end of this "Tillegg" you will find Planck's constant in units of both eVs and Js=Nms. Presently, you will find that it is most practical to use  $h = 4.136 \cdot 10^{-15} \text{ eVs}$ .]

The work function  $W$  (that is, the binding energy for the most loosely bound electrons) for cesium (Cs) and gold (Au) are respectively 1.9 eV and 4.8 eV. Decide whether photoelectric emission is possible when visible light ( $0.4 \mu\text{m} < \lambda < 0.7 \mu\text{m}$ ) is incident on these two metals. [Hint: Show that the photon energies for visible light lie in the range  $1.77 \text{ eV} \lesssim h\nu \lesssim 3.1 \text{ eV}$ .]

**Another small exercise:** A 25-watt light bulb emits around 10% of its effect in the visible region. Estimate roughly the number of photons emitted per second in this  $\lambda$ -region. With night adaptation the eye can see a light source which is so weak that around 5 photons pass the pupil per second. Assume a pupil area of  $\sim 0.5 \text{ cm}^2$ . How far away can the bulb be seen?

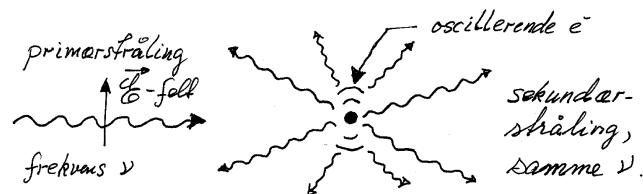
[Hint: Assume that there is no absorption between the bulb and the eye. Since we want only an estimate, you can use a photon energy in the middle of the visible spectrum,  $\lambda = 0.55 \mu\text{m}$ . Answer:  $\sim 2500 \text{ km}$ .]

### 1.3 Compton's experiment (1922–23)

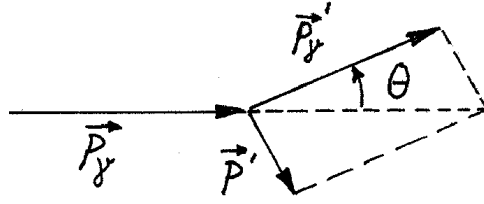


The figure shows a sketch of Compton's experiment. Monochromatic X-rays were scattered on a piece of graphite. The scattered radiation was observed at an angle  $\theta$  which could be varied. The wavelength of this secondary radiation was observed, using so-called Bragg scattering on a calcite crystal. The result was a sensation: Compton observed secondary radiation with a wavelength  $\lambda'$  larger than the primary wavelength  $\lambda$ , and the difference  $\lambda' - \lambda$  (the **Compton shift**) depended on the scattering angle  $\theta$ .

This phenomenon could not be understood in terms of classical electromagnetic theory: If the primary radiation is considered as an electromagnetic wave with wavelength  $\lambda$  and frequency  $\nu = c/\lambda$ , the oscillating electric field in the wave will cause the graphite electrons to oscillate with the same frequency  $\nu$ . According to Maxwell's theory, these oscillating electrons will radiate an electromagnetic wave with the same frequency and hence the same wavelength as that of the primary wave. (This is analogous to the way an electric antenna works.) However, this was not what Compton observed.



It should be noticed that the measurement of  $\lambda'$ , by scattering the secondary radiation on the calcite crystal, is based on the wave nature of the radiation. Compton's result, however, can only be understood by accepting Einstein's hypothesis: Let us consider the process as a collision between a single particle-like light quantum (photon) with energy  $E_\gamma = h\nu = hc/\lambda$  and momentum  $\mathbf{p}_\gamma$  and a single electron which is approximately free, being at rest before the collision. Thus, before the collision the electron has the momentum  $\mathbf{p} = 0$  and the energy  $E = m_e c^2$ . Since the secondary photon leaves the collision with a momentum  $\mathbf{p}'_\gamma$  in the direction  $\theta$  (the so-called scattering angle), we see that the electron necessarily must receive a momentum  $\mathbf{p}' = \mathbf{p}_\gamma - \mathbf{p}'_\gamma$ .



Thus the electron is sent away (“recoils”), with the momentum  $\mathbf{p}'$  and the energy  $E' = \sqrt{m_e^2 c^4 + c^2(\mathbf{p}')^2}$ . This increase of the electron energy of course comes at the expense of the photon energy; the secondary photon must be emitted with a lower energy and a larger wavelength than the primary one, which is precisely what Compton observed.

This increase of the wavelength can be calculated, using the relativistic conservation laws for energy and momentum:

$$\begin{aligned} \frac{hc}{\lambda} + m_e c^2 &= \frac{hc}{\lambda'} + E' & [(E')^2 &= (c\mathbf{p}')^2 + m_e^2 c^4] \\ \mathbf{p}_\gamma + \mathbf{0} &= \mathbf{p}'_\gamma + \mathbf{p}'. \end{aligned}$$

Using these formulae, it is (in principle) a simple matter to show that <sup>1</sup>

$$\lambda' = \lambda + \frac{h}{m_e c} (1 - \cos \theta), \quad (\text{T1.6})$$

which is known as the **Compton relation**. We notice that the **Compton shift**,

$$\lambda' - \lambda = \frac{h}{m_e c} (1 - \cos \theta) \equiv \lambda_C (1 - \cos \theta), \quad (\text{T1.7})$$

is independent of the primary wavelength, but depends on the scattering angle  $\theta$ . <sup>2</sup> After doing this calculation and checking that his experiments agreed with the resulting formula Compton could draw the following dramatic conclusion:

“The present theory depends essentially upon the assumption that each electron which is effective in the scattering scatters a complete quantum (photon). It involves also the

<sup>1</sup>It is easy to derive the Compton relation. We start by solving the above equations for  $E'$  and  $\mathbf{p}'$ , and then calculate  $(E'/c)^2 - (\mathbf{p}')^2$ , which is equal to  $(m_e c)^2$ :

$$\frac{E'^2}{c^2} - (\mathbf{p}')^2 = \left[ m_e c + h \left( \frac{1}{\lambda} - \frac{1}{\lambda'} \right) \right]^2 - (\mathbf{p}_\gamma - \mathbf{p}'_\gamma)^2 = m_e^2 c^2.$$

By writing out the squares (where  $\mathbf{p}_\gamma \cdot \mathbf{p}'_\gamma = p_\gamma p'_\gamma \cos \theta$ ) and using that  $p_\gamma = h/\lambda$  and  $p'_\gamma = h/\lambda'$  you will find that

$$2m_e hc \left( \frac{1}{\lambda} - \frac{1}{\lambda'} \right) + \frac{2h^2}{\lambda \lambda'} (\cos \theta - 1) = 0.$$

The Compton relation follows by multiplying this equation by  $\lambda \lambda' / (2m_e hc)$ .

<sup>2</sup>The quantity  $h/(m_e c) \equiv \lambda_C$  is characteristic for Compton scattering on electrons, and is known as the **Compton wavelength** (for electrons). Its numerical value is

$$\lambda_C \equiv \frac{h}{m_e c} = 2.426\,310\,238(16) \times 10^{-12} \text{ m}.$$

hypothesis that the quanta of radiation are received from definite directions and are scattered in definite directions. The experimental support of the theory indicates very convincingly that a radiation quantum carries with it directed momentum, as well as energy.”

This was a sensational verification of Einstein’s hypothesis:

Light, and other electromagnetic radiation, not only has wave properties (expressed in terms of the wave parameters  $\lambda$  and  $\nu = c/\lambda$ ), but also particle properties, behaving as photons with energy  $h\nu$  and momentum  $h\nu/c = h/\lambda$ .

(T1.8)

What was confusing in 1923, and is still a challenge, is the fact that it is not a question of *either/or* when it comes to wave contra particle properties. What we have to accept, is that light possesses *both* these properties. This is illustrated very clearly by Compton’s experiment, where we have seen that the collision process can be explained in terms of the particle properties, while the measurement of the secondary wavelength is done using diffraction on a crystal. In *this* diffraction process, the periodic structure of the crystal acts as a three-dimensional lattice, causing diffraction maxima in certain directions which depend on the lattice spacing and the *wavelength*. Thus the diffraction depends on the wave nature of the X-rays.

**A small exercise:** Write down the Compton relation for scattering of a photon on a proton. How would you define the Compton wavelength for a proton?

After Compton’s experiment, and the explanation of this, the scientific community was forced to accept that radiation has a dual nature; we have what is called a wave-particle duality. The first step towards the discovery that also particles have such a dual nature, was taken by Niels Bohr.

## 1.4 The Bohr model (1913)

We shall see later (after having learnt a bit of quantum mechanics) that Bohr’s atomic model from 1913 is not an acceptable physical theory. Applied to the hydrogen atom it looked like a success, but for heavier atoms it did not work. In spite of this it is instructive to consider this model a bit more closely. This is because it contains a couple of fundamentally new ideas which still stand as central aspects of quantum mechanics.

First a little bit about the

**A. Background for Bohr’s model:** Three central elements in the historic background for Bohr’s model were

(i) *Balmer’s formula for the visible lines of the hydrogen spectrum.* While the emission spectrum from a solid body is continuous (cf Planck’s radiation law), it was known from early in the 19th century that the radiation from single atoms in a hot gas consists of a set of discrete wavelengths; we have a **line spectrum**. Each atom has its own spectrum, containing wavelengths which are characteristic for the given element. Spectroscopy may therefore be used in chemical analysis.

These spectra actually carry information about the structure of the atoms, and were one of the clues leading to the discovery of quantum mechanics. However, this was not



understood before Niels Bohr entered the picture. An important point here is that there is a system in the distribution of spectral lines. This was discovered by Balmer in 1885, who found that a series of lines belonging to the visible part of the spectrum of hydrogen could be systematized as follows:

$$\frac{1}{\lambda} = R_{\infty} \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, 6.$$

Here,  $R_{\infty}$  is the so-called **Rydberg constant**, which was per 2010 determined experimentally to be<sup>3</sup>

$$R_{\infty} = 10.973\,731\,568\,539(55) \times 10^6 \text{ m}^{-1}.$$

In 1908, Paschen found a series in the infrared region,

$$\frac{1}{\lambda} = R_{\infty} \left( \frac{1}{3^2} - \frac{1}{n^2} \right), \quad n = 4, 5, 6, \dots$$

Today we know that these results for the hydrogen spectrum can be generalized to

$$\frac{1}{\lambda} = R_{\infty} \left( \frac{1}{n^2} - \frac{1}{m^2} \right), \quad n = 1, 2, 3, \dots, \quad m = n + 1, n + 2, n + 3, \dots \quad (\text{T1.9})$$

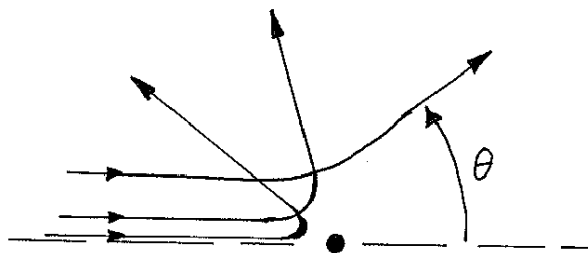
Such a simple empirical formula, covering a large number of lines and containing only one adjustable parameter ( $R_{\infty}$ ) witnesses that there must exist an underlying physical law.

(ii) *Rutherford's model of the atom (1911)*: By bombarding a thin metallic foil with  $\alpha$  particles (helium nuclei), it was discovered in Rutherford's laboratory in Manchester in the years 1908–11 that some of the  $\alpha$  particles were strongly deflected. Rutherford's calculations showed that such a large deflection would be impossible if the positive charge of the metal atoms (and of the  $\alpha$  particles) were distributed fairly evenly over the whole atomic volume. (Such an even distribution of the positive charge was one of the ingredients of Thompson's atomic model, which was popular in those days.) In 1911 Rutherford therefore proposed a new atomic model, with the entire positive charge (and most of the atomic mass) concentrated in a small and very dense atomic nucleus, and with the electrons swirling around in the remaining atomic volume. Thus he assumed that the atom consists mainly of "empty space".<sup>4</sup> With such a small atomic nucleus and with an equally small  $\alpha$  particle (helium nucleus), the repulsive force between the projectile particle and the target particle will be very large when the two particles come sufficiently near each other. This explains why the deflection of the projectile can be very large in some cases (provided that the energy of the projectile is sufficiently high).

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<sup>3</sup>As of 2010, the Rydberg constant was the most accurately determined physical constant.

<sup>4</sup>Today we know that an atomic nucleus in general consists of  $Z$  protons and  $N = A - Z$  neutrons, where  $Z$  is the atomic number,  $A$  is the nucleon number and  $N$  the neutron number. The neutrons were "proposed" by Rutherford (to explain the fact that nuclei have a charge corresponding to  $Z$  protons and a mass corresponding approximately to that of  $A$  protons) and were *discovered* by James Chadwick in 1932. The nuclear radii vary from 1 to 10 femtometer (1 fm =  $10^{-15}$  m) and are approximately given by the empirical formulae  $R_n = k \cdot A^{1/3}$ , where  $A$  is the nucleon number and the empirical coefficient  $k$  lies in the range 1–1.2 fm, depending on how one defines such nuclear "radii". This means that the nuclear radius is roughly a factor 100 000 smaller than the atomic "radius".



(iii) *Planck's quantization condition for the energy transfer between matter and radiation:* The energy is radiated or absorbed in quanta  $h\nu = \Delta E$ , where  $\nu = c/\lambda$  is the frequency of the radiation and  $\Delta E$  is the energy loss or gain for matter.

**B. Bohr's model.** Bohr built his model on the following ideas:

1. The idea of stationary states:

(T1.10)

Bohr assumes that the atom can exist in a discrete set of *states of motion*, each with a *well-defined energy*. This implies, firstly, a **quantization principle**: The energy can only take a discrete set of values. This of course contradicts one of the basic principles of classical physics: In a one-electron atom, e.g., the electron is moving in a  $1/r^2$  force field, and just like for a satellite moving in the field of the earth, a continuum of energies should then be allowed. Secondly, Bohr's assumption breaks with classical physics on another point. Due to the  $1/r^2$  force, the electron is being accelerated the whole time. According to Maxwell's equations, it should then radiate energy continuously, and thus gradually lose its energy, spiralling towards the nucleus. Bohr's assumption implies that no radiation is emitted when the atom is in one of its stationary states, so that the energy is kept constant in such a state. (This is part of the meaning of the word "stationary".)

2. The idea of the quantum leap (or jump):

(T1.11)

With the assumption above, Bohr could interpret the discrete sets of spectral lines as the result of the atoms making sudden **quantum leaps**, jumping between discrete energy levels, and emitting an energy quantum  $h\nu = \Delta E$ , where  $\Delta E$  is the difference between the energies before and after the jump, in agreement with Planck's assumption. For hydrogen, with the observed lines (T1.9), these energy quanta would be

$$h\nu = \frac{hc}{\lambda} = hcR_\infty \left( \frac{1}{n^2} - \frac{1}{m^2} \right), \quad n = 1, 2, 3, \dots, \quad m = n + 1, n + 2, n + 3, \dots$$

Bohr's assumption thus corresponds to the following experimental values for the discrete energy levels of hydrogen:

$$E_n = -hcR_\infty \frac{1}{n^2}, \quad n = 1, 2, \dots$$

Here the numerical value of the constant  $hcR_\infty$  is approximately 13.6 eV.

The two ideas above, of **stationary states** and **quantum jumps**, have turned out to survive; they are central aspects of quantum mechanics. However, in order to explain *why* the atomic energies are discrete, and in order to be able to predict the size of these energies, Bohr introduced two additional assumptions, which turned out to be wrong.

3. *The electron in a hydrogen atom is moving in circular orbits, respecting Newton's laws.* In the hydrogen atom, the potential energy of the electron in the field of the proton is

$$V(r) = -e \frac{e}{4\pi\epsilon_0 r} \equiv -\frac{k}{r}, \quad \text{with } k \equiv \frac{e^2}{4\pi\epsilon_0}.$$

The force on the electron then is

$$\mathbf{F} = -\nabla V(r) = -\frac{e^2}{4\pi\epsilon_0 r^2} \hat{\mathbf{e}}_r$$

where the minus sign means that the force is directed opposite to the unit vector  $\hat{\mathbf{e}}_r$ , that is, towards the proton. For a circular motion, it then follows from Newton's second law that the centripetal acceleration is

$$a = \frac{v^2}{r} = \frac{|\mathbf{F}|}{m_e} = \frac{e^2}{4\pi\epsilon_0 m_e r^2} \equiv \frac{k}{m_e r^2}.$$

It is then straightforward to show that the velocity  $v$ , the angular momentum  $L = mvr$  and the kinetic and total energies  $K$  and  $E$  are proportional to respectively  $r^{-1/2}$ ,  $r^{1/2}$  and  $r^{-1}$ :<sup>5</sup>

$$v(r) = \sqrt{\frac{k}{m_e r}} \propto r^{-1/2},$$

$$L = m_e v r = \sqrt{k m_e r} \propto r^{1/2},$$

$$K(r) = \frac{1}{2} m_e v^2 = \frac{1}{2} \frac{k}{r} \propto 1/r,$$

$$E(r) = K(r) + V(r) \left( = \frac{1}{2} V(r) = -K(r) \right) = -\frac{1}{2} \frac{k}{r} \propto 1/r.$$

This classical calculation allows all values ( $> 0$ ) for the orbital radius  $r$  and ( $< 0$ ) for the energy  $E$ . In order to obtain the all-important energy *quantization*, Bohr therefore needed one more (new and revolutionary) assumption. After some trial and error arrived at the following one:

4. *The angular momentum of the electron must be discretized, and can only be a multiple of  $h/2\pi \equiv \hbar$ , that is,*<sup>6</sup>

$$L = mvr = n\hbar, \quad n = 1, 2, \dots.$$

According to the relations above, such a quantized angular momentum corresponds to quantized values also for the radius and the energy:

$$L = \sqrt{k m_e r} = n\hbar \implies r = r_n = \frac{n^2 \hbar^2}{k m_e} = n^2 \frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e} \implies$$

<sup>5</sup>Note that with another definition of the coefficient  $k$ , these calculations also hold for a satellite moving in a circular orbit around the earth.

<sup>6</sup>In modern quantum mechanics, the quantity  $h/2\pi \equiv \hbar$  ("h-bar") occurs much more frequently than Planck's constant  $h$  itself.

$$E_n = -\frac{k}{2r_n} = -\frac{k^2 m_e}{2\hbar^2} \frac{1}{n^2} = -\frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 m_e c^2 \frac{1}{n^2}, \quad n = 1, 2, \dots$$

In the formula for the energies, the quantity

$$m_e c^2 = 510\,998.910(13) \text{ eV} \approx 0.511 \text{ MeV} \quad (\text{electron rest energy})$$

has the dimension of an energy. This means that the quantity in parantheses must be a dimensionless constant. This constant plays a very important role in quantum physics, and is called the **fine-structure constant**:

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137.035\,999\,679(94)} \quad \left( \begin{array}{c} \text{fine-structure} \\ \text{constant} \end{array} \right). \quad (\text{T1.12})$$

Inserting numbers, we now find that the lowest energy according to Bohr's theoretical model is

$$E_1 \approx -13.6 \text{ eV},$$

corresponding precisely to the lowest experimental energy (the “ground-state” energy).

Also the smallest radius (of the ground state) does in fact play an important role in quantum mechanics (as we shall see later) and is called the **Bohr radius**:

$$a_0 \equiv \frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e} = 0.529\,177\,208\,59(36) \times 10^{-10} \text{ m} \quad (\text{Bohr radius}). \quad (\text{T1.13})$$

What was very sensational with Bohr's model was that he was able to “explain” the  $1/n^2$  dependence of the experimental hydrogen energies *without introducing any new parameter* — Planck's constant did the job not only for light, as Planck and Einstein had found, but also for the atom. When Einstein was told about this new theory, he exclaimed: “Then this is one of the greatest discoveries”. (Since then we have learnt that Planck's constant *always* enters in quantum mechanics, whether we consider particles or radiation, or both for that matter.)

Now we must hasten to add that in spite of this success, assumptions number 3 and 4 in Bohr's theory have turned out to be wrong. It *is* correct that the angular momentum is quantized, and it even turns out that  $\hbar$  plays an important role in this quantization. However, the ground state turns out to have zero angular momentum (not  $\hbar$  as in Bohr's model). What is even more important is that the notion of classical orbits for the electrons has to be discarded. Thus, to explain the stationary states of e.g. the hydrogen atom, we are today using a quantum-mechanical theory where the **wave nature** of the particles plays the central role.

The classical-mechanical way of thinking (which is so tempting for all of us), where the particle has a well-defined orbit  $\mathbf{r} = \mathbf{r}(t)$ , is wrong when it comes to phenomena on the atomic or sub-atomic scale.

It took several years after Bohr's discovery in 1913 before this became clear. It was soon found that the theory ran into difficulties when applied to atoms with more than one electron. Thus, the theory had little "predictive power" (and that is a bad sign for any physical theory). However, it took many years to realize that the theory had to be given up altogether. The decisive step came with

## 1.5 de Broglie's hypothesis (1923)

Soon after the confirmation of the **wave-particle duality** of light by Compton's experiment, the French physicist Louis de Broglie came up with a revolutionary proposal: What if also particles possess a wave-particle duality, with the same relation between wave and particle parameters as for light (proposed by Einstein)? :

$$\boxed{\lambda = \frac{h}{p}, \quad \nu = \frac{E}{h}} \quad (\text{de Broglie's hypothesis}). \quad (\text{T1.14})$$

de Broglie's proposal implied that a particle with momentum  $p$  and energy  $E$  should have some kind of wave behaviour, corresponding to a wavelength  $\lambda$  and a frequency  $\nu$ .

de Broglie's hypothesis was not taken seriously. Einstein was one of the few who considered it as an interesting idea. However, de Broglie felt that his idea was supported by the following fact: If one requires that Bohr's circular orbit cover an integer number of wavelengths,

$$2\pi r = n\lambda = nh/p, \quad n = 1, 2, \dots,$$

then it follows that

$$(L =) pr = \frac{nh}{2\pi} = n\hbar,$$

which reproduces Bohr's quantization condition.

As we shall see, in spite of the skepticism de Broglie's hypothesis was the starting point of a whole avalanche of discoveries, nothing less than a scientific revolution. During a hectic period of 2–3 years (1924–27) the hypothesis was confirmed, through the development of quantum mechanics as a physical theory and through experimental verifications. The change of paradigm which started with the work of Planck, Einstein and Bohr, was completed in these years.

The first *direct* experimental verifications of de Broglie's hypothesis were found in 1926–27 by Davisson and Germer and by Thomson (see footnote page 15 in Hemmer, and see chapter 1 in B&J). D & G scattered electrons on a nickel crystal, and observed that the scattered intensity showed a strong variation with the angle, in analogy with what we see when X-rays are scattered on a three-dimensional crystal lattice. These variations could be explained by associating with the electrons a wavelength given by de Broglie's proposal, much the same way as we explain X-ray scattering on a crystal.

However, before this experimental verification there was an important theoretical breakthrough by the Austrian physicist Erwin Schrödinger, who decided to try to find a *wave equation* for "de Broglie's waves". Towards the end of 1925 he succeeded in finding a wave equation which turned out to reproduce Bohr's results for the energy levels of the hydrogen atom.

Unlike Bohr's theory, Schrödinger's wave equation turned out to have large predictive power; it described heavier atoms well and also worked for other systems. In fact, this equation plays a role in quantum mechanics which is comparable to the role played by Newton's second law in classical mechanics. This became clear almost immediately, and proved that de Broglie was right: Particles have wave properties in addition to their particle properties.

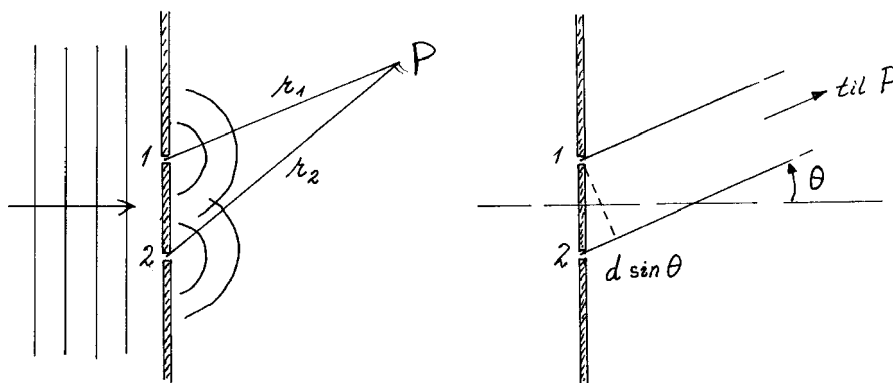
Before introducing this equation, we shall consider an experiment which gives a very direct proof of the wave nature of particles, namely a two-slit experiment with electrons. This experiment played absolutely no role in the historical development of quantum physics; it was performed as late as in 1961. It is included here because it demonstrates the wave nature much more clearly and is much easier to interpret than Davisson and Germers experiment.

## 1.6 The wave nature of particles

The wave nature — both of light and particles — can be illustrated very clearly by so-called double-slit experiments. We shall look more closely at some experiments of this kind, because they in a very direct way challenge our classical (and “macroscopic”) way of thinking, and illustrate the difference between classical and quantum physics.

### 1.6.a A double-slit experiment with surface waves in water

(*not* very challenging, but used to introduce some concepts).



A wave with wavelength  $\lambda$  is incident on a “dam” with two openings 1 and 2, with a width  $b (\ll \lambda)$  and a distance  $d$  apart.

With 1 or 2 open we observe at the point  $P$  (far away from the openings) a **a wave “height”** (or wave function)

$$h_i = A(\theta) \cos(kr_i - \omega t), \quad (i = 1, 2),$$

where  $A(\theta)$  is a slowly varying function of  $\theta$ . This function decreases with the distance as  $1/\sqrt{r}$ . The **intensity** (the energy flux) then is proportional to  $1/r$ :

$$I_i \propto \overline{h_i^2}^t \propto 1/r,$$

as it should be for this wave which is spreading out as “half circles” (from opening 1 or 2). Note that the intensity is proportional to the square of the wave height (wave function),

averaged over time. This wave function is a solution of the wave equation for surface waves in water.

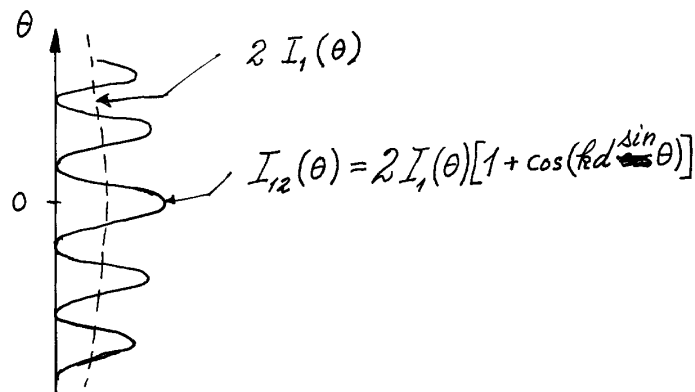
This wave equation for surface waves is approximately **linear** for small wave heights. Therefore, if we let *both* 1 and 2 be open, the resulting wave height (wave function) at the point  $P$  will be given approximately by the sum of  $h_1$  and  $h_2$  (cf the **superposition principle**):

$$h_{12} \approx h_1 + h_2 = A(\theta)[\cos(kr_1 - \omega t) + \cos(kr_2 - \omega t)].$$

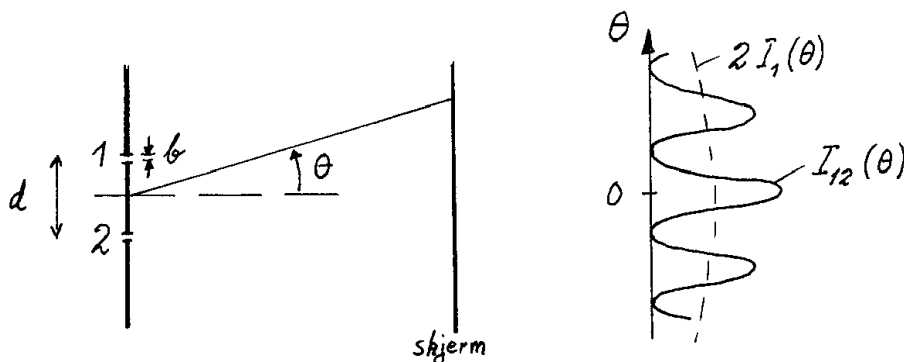
As you know, we then get an interference pattern behind the dam, with constructive interference ( $h_{12} = 2h_1$  and  $I_{12} = 4I_1$ ) where the path difference between the two waves is an integer number of wavelengths,

$$r_2 - r_1 = d \sin \theta = n\lambda,$$

and destructive interference ( $h_{12} = 0$  and  $I_{12} = 0$ ) where  $d \sin \theta = (n + \frac{1}{2})\lambda$ . (See the figure.)



### 1.6.b A double-slit experiment with monochromatic light (Young, 1802)



With  $b \ll \lambda$  and 1 or 2 open we again get slowly varying intensity distribution  $I_i(\theta)$  (see the dashed line in the figure). With both 1 and 2 open, we get the same behaviour of  $I_{12}$  as for the water waves (solid line in the figure). Based on such an experiment, Young concluded in 1802 that light must be a wave phenomenon. This was a decisive blow against Newton's

corpuscular theory of light, which had been dominating for a century. We should note that Young was not able to decide *what kind* of wave this was. It took sixty years before it was understood by Maxwell that the interference and diffraction effects observed by Young and Fresnel (and others) could be understood in terms of interference of electromagnetic waves, and that the wave functions which then interfere are classical electromagnetic fields.

Long after Young (well into the last century in fact) it was discovered that this kind of experiment can also be used to demonstrate the non-classical **particle nature** of light: If the intensity of the incident light is gradually decreased, the intensity distribution  $I_{12}(\theta)$  on the screen of course also decreases in the same way, but the *form* of this distribution is the same, as long as we are able to observe it. At some point it becomes invisible to our eyes, but it can still be observed, e.g. by the use of a photographic plate and sufficiently long exposure time. (This technique is used in astronomy to observe very distant and faint light sources.) A single photon can then darken a point on the plate. Such a system works even if the intensity is so low that we register only one photon per day (e.g.). This way, the particle nature of light becomes very evident.

The fact that a single photon is registered at some definite point on the plate (instead of being “smeared out” in any manner), in a way does not agree with the classical wave theory, which predicts an intensity distribution  $I_{12}(\theta)$ . This is an unavoidable consequence of the particle nature of light, which clearly is a quantum (as opposed to classical) phenomenon.

Thus wave theory can not predict what happens with a single photon (or with two, or with three,...). We need to collect a large number of photons before we begin to see that the interference pattern emerges. Thus we can conclude that:

The classical interference pattern  $I_{12}(\theta)$  is valid in the sense that it gives the **probability distribution** of the photons on the screen (suitably normalized). The probability of observing a single photon at an angle  $\theta$  then is

(T1.15)

$$P(\theta) \propto I_{12}(\theta).$$

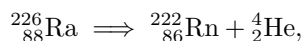
With this **probability interpretation** of the classical wave theory, there is no contradiction between the wave properties and the particle properties of light. Both properties are present. The wave property determines the interference (both here and in scattering on a grating or on a crystal). The particle property shows up in the detection, and also in e.g. Compton scattering.

This probability theory, as already stated, does not allow us to predict what happens with a single photon. And there is no other theory that can help us with this. Thus the photons, which do not differ in any way, experience unpredictable and different fates behind the double-split screen. This element of arbitrariness or unpredictability is a central feature of quantum physics, which most of us have some difficulties in accepting.<sup>7</sup>

This has been the source of much debate through the years. Einstein, for example, who was one of the fathers of quantum theory, could never reconcile himself with this feature of

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<sup>7</sup>The unpredictability feature of quantum physics is also evident if we observe an ensemble of  $\alpha$ -radioactive nuclei, e.g. of the isotope  $^{226}\text{Ra}$ . These unstable nuclei, which decay by emitting an  $\alpha$  particle (helium nucleus),





quantum mechanics. He is often cited for the following statement: “God does not throw dice”. There have been many attempt to modify the theory to remove the unpredictability. (Keywords here are “hidden variables” and Bell’s inequalities.) So far, it seems that this element of quantum mechanics can not be removed. It is something we have to live with.

### 1.6.c A double-slit experiment with electrons

The double-slit experiment with electrons played absolutely no role in the development of quantum mechanics, but is included here because it shows the wave nature of particles very clearly.<sup>8</sup>

In order to get an interference pattern for visible light one needs to work with a slit width comparable with the wavelength, that is,  $\lesssim 1$  micrometer. If one wants to make a similar experiment with particles, much smaller slit widths are required than for light, and similarly for the distance  $d$  between the slits. This is because the de Broglie wavelength for particles are very small. Thus, for non-relativistic electrons we find from de Broglie’s formula a wavelength

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_e E_{kin}}} = \frac{h}{m_e c} \sqrt{\frac{m_e c^2}{2E_{kin}}} = \lambda_C \sqrt{\frac{511000 \text{ eV}}{2E_{kin}}},$$

that is,

$$\lambda = \frac{h}{p} = 12.264 \text{ \AA} \sqrt{\frac{1 \text{ eV}}{E_{kin}}} \quad \left( \begin{array}{l} \text{de Broglie wavelength} \\ \text{for non-rel. electrons} \end{array} \right). \quad (\text{T1.16})$$

Even with a kinetic energy as small as 1 eV, the de Broglie wavelength thus is as small as 12 Å. *So* slow electrons are very difficult to handle experimentally. In practice one must therefore work with faster electrons, with wavelengths which are even smaller. This is why the first double-slit experiment with electrons that I have heard about was done as late as in 1961 (C. Jönsson).

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are completely identical. Still they do not decay simultaneously. We can measure the average lifetime, which is 1620 years, and we can observe the distribution of the lifetimes. But we can not predict how long a single nucleus will survive. Starting out with a large number, we can state that the expected number (surviving) after 1620 years is reduced by a factor  $1/e$ . After another 1620 years the number is reduced by another factor  $1/e$ . In fact at any point in time, the laverage lifetime of those who have survived is 1620 years. Thus, there is no difference between those who died early and those who survive for a long time. This of course is not very easy to understand intuitively.

<sup>8</sup>As mentioned earlier, the wave nature of electrons was demonstrated in experiments carried out in 1926–27 by Davisson & Germer and by G.P. Thomson.

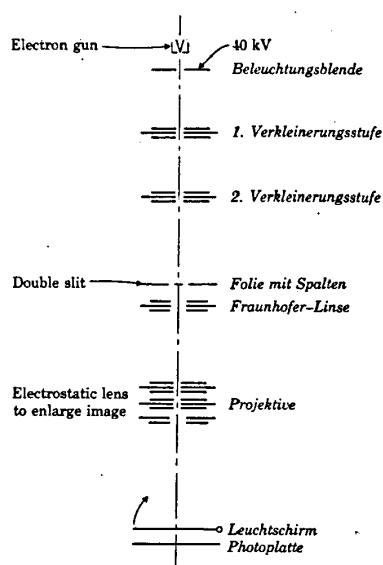


Figure 24-10. C. Jönsson's experimental arrangement for obtaining double slit interference pattern of electrons. [C. Jönsson, *Z. Phys.*, 161 (1961)]

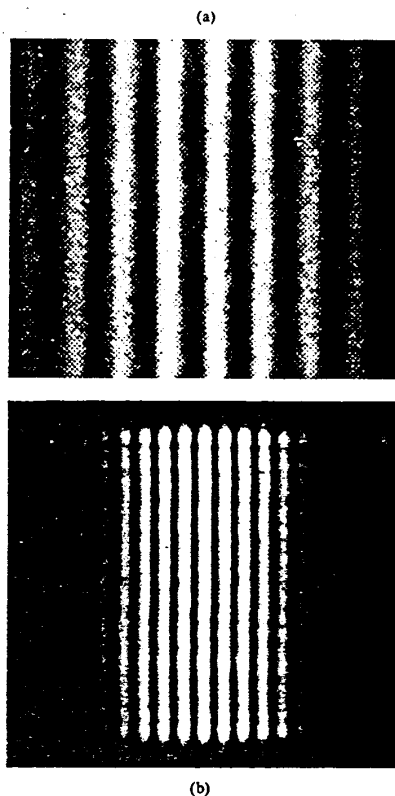


Figure 24-11. (a) A double slit interference pattern of electrons. Each grain in the photographic negative is produced by a single electron. For comparison, (b) is the double slit interference pattern of light shown in Figure 22-17. In this photo, each grain in the negative is produced by a single photon. [Photo (a) by Professor C. Jönsson, University of Tübingen]

The result of that experiment is the same as for light: With one of the slits open one gets a broad intensity distribution  $I_1(\theta)$ . With both slits open, one observes an interference pattern, and this pattern is the same whether one uses a very high flux of incoming electrons or let the electrons come one by one. (See the figure above.) Thus for certain values of  $\theta$  no electrons are observed (that is, fewer than with only one slit open), while for other values one gets up to four times as many as with only one slit open.

The only possible explanation of this interference pattern in the electron distribution is that we again with a wave phenomenon. By measuring the distance between the interference minima, one can find the wavelength  $\lambda$  of these waves. This wavelength comes out in agreement with de Broglie's formula.

The question then is: What kind of waves are interfering in this case? Here we find ourselves in the same situation as Young and Fresnel in the early 1800s. These gentlemen did not know that the light in Young's experiment could be associated with classical electromagnetic waves and that the wave function was the electric field. Therefore they had to invent abstract wave functions, which were added and squared to obtain the observed intensity distribution  $I_{12}(\theta)$ .

That is precisely what *we* are now forced to do for the electrons: With the beam of electrons which are incident on the two-slit screen from the left we associate an abstract

wave function, a plane harmonic wave <sup>9, 10</sup>

$$\Psi = C \exp[2\pi i(\hat{\mathbf{k}} \cdot \mathbf{r}/\lambda - \nu t)] = C \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] = C \exp[i\mathbf{p} \cdot \mathbf{r} - Et]/\hbar.$$

Behind the two slits we will then have two (equally abstract) cylindrical waves,

$$\Psi_i = A(\theta)e^{i(kr_i - \omega t)}, \quad i = 1, 2.$$

By superposing these and taking the absolute square,

$$|\Psi_{12}|^2 = |\Psi_1 + \Psi_2|^2,$$

we get a function which reproduces the form of the observed interference pattern.

Again we note that each electron is observed at some point (e.g. darkening a point on a photographic plate). A single electron gives no interference pattern, only one point. The interference pattern emerges only after a large number of electrons have passed the slits. (See, e.g. the illustration p 18 in Hemmer, or p 54 in B&J.) Thus our abstract wave function does not predict where a single electron will be observed. However, this wave function leads to the correct probability distribution  $P(\theta) \propto |\Psi_{12}|^2$ , in analogy with the situation for light.

Thus, the *bad* news is that we are forced to accept a theory which gives **probabilistic predictions**. The *good* news is that light quanta and particles at least in this context seem to behave much the same way. (However, here we must hasten to add that when we study this in more detail, there are very significant differences between the quantum-mechanical descriptions of light and matter.) Thus, for electromagnetic radiation, Maxwell discovered that Young's abstract wave function could be replaced by the electric field, which is in principle a measurable quantity (for macroscopic fields). For particles, it turns out that the wave function  $\Psi$  introduced above can not be measured.

We must therefore get used to the fact that the wave function  $\Psi$  is an *abstract quantity*, which exists only in our *theoretical description*, and which is not a part of the physical system we are considering. (T1.17)

Is the electron a wave or a particle? The answer is that it has *wave nature*, e.g. in the sense described above. But it also has a particle nature, which manifests itself e.g. when we try to observe it, for example with the photographic plate, or in some other way. Thus, for electrons (and other particles) we have a wave-particle duality, similar to that found for photons.

<sup>9</sup>We shall explain later why we this time are using a complex wave function, instead of cosine or a sine.

<sup>10</sup>Expressed in terms of the wave number  $k$  and the angular frequency  $\omega$ , de Broglie's hypothesis,  $\lambda = h/p$  and  $\nu = E/h$ , can be stated on the simple form

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} \equiv \frac{p}{\hbar}, \quad \omega = 2\pi\nu = \frac{2\pi E}{h} = \frac{E}{\hbar},$$

where

$$\hbar \equiv \frac{h}{2\pi} \quad (\text{"h-bar"}).$$

The direction of propagation  $\hat{\mathbf{k}}$  is the direction of the incoming electron beam:  $\mathbf{p} = p\hat{\mathbf{k}} = \hbar k \hat{\mathbf{k}} \equiv \hbar \mathbf{k}$ .

Does each single electron pass through one of the slits or through both? Here it is difficult to give a clear answer. What can be stated with certainty, is that both slits have to be open if we want to observe the interference pattern  $I_{12}(\theta) \propto |\Psi_{12}|^2$ . It is also a fact that nobody has observed “half” electrons (or “half” photons). Thus there is no indication that the electron can be divided into two parts, one part travelling through slit 1 and the other through slit 2. We can of course modify our experiment so that we monitor whatever passes through slit 1 and 2. Experiments (with one electron at a time) then show that the electron either passes through 1 or 2, not through both at the same time. However, with an experiment which allows such a monitoring, it turns out that there is no interference pattern; we get the same smooth distribution as with only one open slit. Thus we have to conclude that in an experiment where the interference pattern is observed, we are not able to answer the question about which slit the electron passed.

This is only one of many examples where questions which seem to be perfectly reasonable according to classical physics and our “macroscopic” way of thinking, can not be answered in the submicroscopic and quantum-mechanical world.

### A small exercise:

**a.** Calculate the de Broglie wavelength  $\lambda$  for electrons with a kinetic energy of 200 eV. [Answer: 0.8762 Å.]

**b.** Suppose that electrons in an old-fashioned TV tube have a kinetic energy 20 keV, that is a factor 100 higher than in the previous question. What is then the (non-relativistic result for) the wavelength in this case? [Answer: A factor 10 smaller than in the previous case.]

**c.** Use the *relativistic* formula  $p = \sqrt{E^2/c^2 - m_e^2 c^2}$  (where  $E = E_{kin} + m_e c^2$ ) to show that the ratio between the relativistic (i.e. correct) value of the momentum  $p$  and the non-relativistic one ( $p = \sqrt{2m_e E_{kin}}$ ) is  $\sqrt{1 + E_{kin}/2m_e c^2}$ . How big is the relative error of the wavelength in question **b**? [Answer: The correct value for the wavelength is about 1 percent smaller than the value found in question **b**.]

## 1.7 Wave equations. Motivation for Schrödinger’s equation

Surface waves in water are described by a certain wave equation. Radio waves, light waves and other electromagnetic waves are in general described by the so-called classical wave equation, which can be deduced from Maxwell’s equations. It is then natural to pose the following question (as Schrödinger did in 1925): What is the wave equation that has de Broglie’s harmonic waves as solutions?

### 1.7.a Free particle, with sharp momentum $\mathbf{p} = \hat{\mathbf{e}}_x p_x + \hat{\mathbf{e}}_y p_y + \hat{\mathbf{e}}_z p_z$ and energy $E = \mathbf{p}^2/2m$

For a free particle, with well-defined momentum  $\mathbf{p}$  and energy  $E = \mathbf{p}^2/2m$  — e.g. the electrons incident on the two-slit screen — we shall see that it is easy to find a suitable wave equation. We saw that de Broglie's hypothesis,

$$\mathbf{k} = \mathbf{p}/\hbar \quad \text{and} \quad \omega = E/\hbar, \quad (\text{de Broglie's hypothesis}) \quad (\text{T1.18})$$

corresponds to a plane, harmonic wave with the form

$$\Psi(\mathbf{r}, t) \propto e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} = e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} = e^{i(p_x x + p_y y + p_z z - Et)/\hbar}.$$

Like Schrödinger we can ask ourselves: What is the simplest differential equation that is satisfied by this plane wave  $\Psi$ ? To find the answer, we shall introduce a few mathematical **operators** which turn out to play central roles in quantum mechanics, namely

$$\hat{p}_x \equiv \frac{\hbar}{i} \frac{\partial}{\partial x}, \quad \hat{p}_y \equiv \frac{\hbar}{i} \frac{\partial}{\partial y} \quad \text{and} \quad \hat{p}_z \equiv \frac{\hbar}{i} \frac{\partial}{\partial z}. \quad (\text{T1.19})$$

#### A small exercise:

**A)** When an operator acts on a function, the result usually is a *new* function. As an example, you should let the operator  $\partial/\partial x$  act on the functions  $\exp(-x^2)$ ,  $\sin kx$  and  $\cos kx$ .

**B)** In some cases you will find that an operator acting on some function results in the same function multiplied by a constant. This function is then called an **eigenfunction** of the operator in question, and the constant is called an *eigenvalue* of the operator. As an example, show that  $\exp(ikx) [= \cos kx + i \sin kx]$  is an eigenfunction of the operator  $\hat{p}_x = (\hbar/i)\partial/\partial x$ , and find the eigenvalue.

**C)** Show that the function  $e^{-x^2/2}$  is an eigenfunction of the operator  $\hat{h} = -\frac{1}{2}d^2/dx^2 + \frac{1}{2}x^2$  and determine the eigenvalue.

Applying the operator  $\hat{p}_x$  on the function  $\Psi$ , we see that

$$\hat{p}_x \Psi = \frac{\hbar}{i} \frac{\partial}{\partial x} e^{i(p_x x + p_y y + p_z z - Et)/\hbar} = \frac{\hbar}{i} \frac{i p_x}{\hbar} \Psi = p_x \Psi. \quad (\text{T1.20})$$

This equation is a so-called **eigenvalue equation**, on the form

$$\text{Operator} \cdot \Psi = \text{eigenvalue} \cdot \Psi. \quad (\text{T1.21})$$

It states that the function  $\Psi$  is an **eigenfunction** of the operator  $\hat{p}_x$  with an **eigenvalue** equal to the momentum component  $p_x$ . In the same manner, we find that

$$\hat{p}_y \Psi = p_y \Psi, \quad \hat{p}_z \Psi = p_z \Psi \quad \text{and} \quad \hat{\mathbf{p}} \Psi = \mathbf{p} \Psi,$$

where <sup>11</sup>

$$\hat{\mathbf{p}} \equiv \hat{\mathbf{e}}_x \frac{\hbar}{i} \frac{\partial}{\partial x} + \hat{\mathbf{e}}_y \frac{\hbar}{i} \frac{\partial}{\partial y} + \hat{\mathbf{e}}_z \frac{\hbar}{i} \frac{\partial}{\partial z} \equiv \frac{\hbar}{i} \nabla \quad \text{and} \quad \mathbf{p} = \hat{\mathbf{e}}_x p_x + \hat{\mathbf{e}}_y p_y + \hat{\mathbf{e}}_z p_z. \quad (\text{T1.22})$$

<sup>11</sup>Here,  $\hat{\mathbf{e}}_x$  etc are unit vectors, while the “hat” over  $\mathbf{p}$  means that  $\hat{\mathbf{p}}$  is an operator.

These eigenvalue equations play a very important role in quantum mechanics, and you should bear them in mind:

de Broglie's abstract plane harmonic wave  $\Psi$ , which "describes" a particle (or particles) with sharply defined momentum  $\mathbf{p}$ , with components  $p_x, p_y, p_z$ , is an eigenfunction of the operators  $\hat{\mathbf{p}}, \hat{p}_x, \hat{p}_y, \hat{p}_z$ . The eigenvalues are the sharp momentum values  $\mathbf{p}, p_x, p_y, p_z$ .

(T1.23)

We call these operators **momentum operators**. We can also introduce an **energy operator**,

$$\hat{H} \equiv \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} = \frac{\hat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2m} \nabla^2,$$

which if possible plays an even more central role in the theory. Since  $\hat{p}_x^2 \Psi = \hat{p}_x(p_x \Psi) = p_x^2 \Psi$ , we obviously have

$$\hat{H} \Psi = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \Psi = E \Psi.$$

Thus  $\Psi$  is an eigenfunction of the operator  $\hat{H}$  with the (kinetic) energy as eigenvalue. During this course, we shall get very well acquainted with the energy operator, which is in general called the Hamilton operator, or simply the **Hamiltonian**. (Therefore the symbol  $\hat{H}$ .)

We should also notice that  $\Psi$  [proportional to  $\exp(-iEt/\hbar)$ ] is an eigenfunction of the operator  $\partial/\partial t$ :

$$\frac{\partial}{\partial t} \Psi = -\frac{iE}{\hbar} \Psi.$$

Including an extra factor  $i\hbar$ , we see that

$$i\hbar \frac{\partial}{\partial t} \Psi = E \Psi.$$

Thus, comparing with the relation  $\hat{H} \Psi = E \Psi$ , we discover (as Schrödinger did) that de Broglie's plane wave  $\Psi$  satisfies the following partial differential equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi.$$

( Schrödinger's equation  
for a free particle ) (T1.24)

This is the **Schrödinger equation** for a free particle, the *simplest* equation satisfied by de Broglie's plane waves. It has turned out that this simplest equation is also the one that *works* (in non-relativistic quantum mechanics).

An important point is to note how the imaginary unit  $i$  entered in the "derivation" above. We note that the appearance of the factor  $i$  is an unavoidable consequence of the fact that the non-relativistic energy-momentum relation  $E = \mathbf{p}^2/2m$  is linear in  $E$  and quadratic in  $\mathbf{p}$ . This is what leads to a complex wave equation and complex de Broglie waves. The real and imaginary parts of de Broglie's wave  $\Psi$  do not satisfy this equation separately. Thus we are forced to work with a complex wave function.

The equation above is easily generalized to a case where the particle is moving in a constant potential  $V$ , so that<sup>12</sup>

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V \quad (V = \text{constant}).$$

Following de Broglie's recipe, we again set  $\Psi = \exp[i(\mathbf{p} \cdot \mathbf{r} - Et)/\hbar]$ , and find that  $\Psi$  now is an eigenfunction of the Hamiltonian  $\widehat{H} = -(\hbar^2/2m)\nabla^2 + V$ ,

$$\widehat{H}\Psi = \left( -\frac{\hbar^2}{2m}\nabla^2 + V \right) \Psi = E\Psi,$$

while

$$i\hbar \frac{\partial \Psi}{\partial t} = E\Psi,$$

as before. Thus, the plane wave  $\Psi$  in this case satisfies the following Schrödinger equation:

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

We note that the recipe for arriving at the Hamiltonian

$$\widehat{H} = \frac{\widehat{p}_x^2 + \widehat{p}_y^2 + \widehat{p}_z^2}{2m} + V = -\frac{\hbar^2}{2m}\nabla^2 + V$$

is as follows: Express the classical energy ( $K + V$ ) in terms of coordinates and momenta. Then replace the momentum  $p_x$  by the corresponding momentum operator  $\widehat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$ , etc.

### 1.7.b Particle influenced by a force $\mathbf{F}(\mathbf{r}) = -\nabla V(\mathbf{r})$

Here, Schrödinger was faced by a challenge. In a force field, a particle with well-defined energy  $E$  will have a variable momentum

$$|\mathbf{p}(\mathbf{r})| = \sqrt{2m[E - V(\mathbf{r})]},$$

according to classical mechanics. de Broglie's recipe then becomes useless; the definition of a wavelength requires a harmonic wave, which is relevant only in force-free space. Schrödinger proposed the following way out of this problem: Let us try with a wave equation with the same form as above,

$$i\hbar \frac{\partial \Psi}{\partial t} = \left( -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right) \Psi \equiv \widehat{H}\Psi \quad (\text{Schrödinger's equation}),$$

(T1.25)

where now  $V(\mathbf{r})$  now depends on  $\mathbf{r}$ . Schrödinger at once went ahead to test this simple *hypothesis*, today known as the **(time-dependent)** Schrödinger equation, by applying it to the fundamental question of atomic physics at that time:

What is it that keeps atoms from "imploding", in the sense that the electrons "fall in" towards the nucleus, because of the attraction between positive and negative charges?

<sup>12</sup>In quantum mechanics it is customary to refer to the potential energy simply as the potential.

More specifically, what is it that keeps the electron of the hydrogen from "falling" into the proton, under continuous emission of radiation, ending up with an "atom" with the same size as the proton ( $\sim 10^{-15}$  m), as we would expect from classical mechanics and classical electrodynamics?

The Schrödinger equation turned out to be the answer to this and many more questions connected to quantum physics, and it did not take long before **quantum mechanics** was established as a physical theory.

In 1925, before Schrödinger's work, it was clear that Bohr's idea about **stationary states** with **quantized energies** e.g. for the hydrogen atom could be regarded as an **experimental fact**. In each such state the energy of the hydrogen atom is well-defined (sharp), given by one of the values

$$E_n = -\frac{1}{2}\alpha^2 \frac{m_e c^2}{n^2}, \quad n = 1, 2, 3, \dots \quad (\text{T1.26})$$

The state with the lowest energy,  $E_1 = -13.6$  eV, is called the **ground state**. A hydrogen atom can stay in the ground state forever, if it is not disturbed. But atoms can also be **excited**, e.g. to the first excited energy level,  $E_2 = E_1/4 \approx -3.4$  eV, by radiation with photons with suitable energy  $h\nu = E_2 - E_1$ , or via thermal excitation (hot gas). Excited atoms will sooner or later jump back to lower-lying levels, under the emission of photons carrying the excess energy. As an example, Balmer's spectral lines are due to transitions between the levels  $E_n$  and the level  $E_2$  (corresponding to photons in the visible region of the spectrum). Such transitions happen suddenly, in agreement with Bohr's idea of **quantum jumps**.

Equally clear in 1925 it was that the remaining aspects of Bohr's model were not valid. In particular, the idea of circular (and later elliptical) orbits had turned out to be unsuccessful for atoms with more than one electron. It was therefore natural for Schrödinger to investigate if his wave equation could be applied to atoms.

Schrödinger attacked the hydrogenatom (the simplest one), which somewhat simplified can be considered as an electron of mass  $m_e$  moving in the electrostatic field from the "approximately infinitely heavy" proton. This field corresponds to an electrostatic potential  $U(r) = e/(4\pi\epsilon_0 r)$ . The potential energy of the electron (simply called the potential in quantum mechanics) then is<sup>13</sup>

$$V(r) = -eU(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \quad (\text{Coulomb potential}).$$

Schrödinger started by searching for solutions of the eigenvalue equation

$$\boxed{\widehat{H}\psi(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})} \quad \left( \begin{array}{l} \text{Schrödinger's time-} \\ \text{independent equation} \end{array} \right),$$

(T1.27)

which is known as **Schrödinger's time-independent equation**. For each such energy eigenfunction  $\psi(\mathbf{r})$  that can be found, it is easy to see that the function

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

<sup>13</sup>We choose to set the potential equal to zero at  $r = \infty$ . This means that bound states correspond to a negative potential energy, and also to a negative total energy  $E = K + V$ .



satisfies the time-dependent Schrödinger equation. [Check this.] To find these eigenfunctions ( $\psi(\mathbf{r})$ ) is a purely mathematical task, which Schrödinger solved readily, and which we too shall solve not as fast later in this course.

It turns out that the equation above has eigenfunction solutions for *all* energies  $E > 0$ . For negative energies, on the other hand (corresponding to bound states of the electron and the proton), Schrödinger found that this equation has energy eigenfunction solutions only for a **discrete set of energy eigenvalues**, and this set turned out to be precisely the set of "experimental" energies mentioned above!

We shall study these solutions in great detail later in the course, so let us here try only to convey a rough idea about how the **quantum-mechanical description** of the hydrogen atom works. For the lowest energy,  $E_1 = -13.6 \text{ eV}$ , Schrödinger found one eigenfunction of the energy operator  $\widehat{H}$ , on the form

$$\psi_1(r) = C_1 e^{-r/a_0} \quad \text{with} \quad a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e} = \text{Bohr radius.} \quad (\text{T1.28})$$

As we have seen above, this means that the wave function

$$\Psi_1(r, t) = C_1 e^{-r/a_0} e^{-iE_1 t/\hbar} \quad (\text{T1.29})$$

is a solution of Schrödinger's time-dependent equation. Thus the radius  $a_0$  of Bohr's innermost circular orbit plays a role also in Schrödinger's solution. We note that this is a very different role.

Here,  $r$  is the distance from the proton to the electron. We note that this wave function is spherically symmetric (depends on  $r$  but not on angles). The time dependence is given by the factor  $\exp(-iE_1 t/\hbar)$ , which is a complex number running around the complex unit circle, with absolute value  $|\exp(-iE_1 t/\hbar)| = 1$ . The spatial factor  $e^{-r/a}$  has its maximal value when the distance  $r$  is equal to zero. It is important to note that Schrödinger's time-independent equation has no eigenfunction with a lower energy than  $E_1$ . For the next lowest energy,  $E_2 \approx -3.4 \text{ eV}$ , Schrödinger found four independent eigenfunctions. Three of these depend both on  $r$  and on the angles  $(\theta, \phi)$ .

Thus, Schrödinger found that his time-dependent equation has a special set of solutions, on the form  $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-iEt/\hbar}$ , which implies that these are also eigenfunctions of the energy operator  $\widehat{H}$ . It was of course very promising that the energy eigenvalues are precisely the discrete energies which are observed *experimentally* for the stationary hydrogen states. These are simple mathematical facts, which may be somewhat unfamiliar for us presently, but which are easy to digest when we get some more experience.

It was much more challenging in 1925 (and still is) to come to grips with the *physical interpretation* of these mathematical facts. We understand that the strange wave-function solution  $\Psi_1(r, t)$  of Schrödinger's time-dependent wave equation must have something to do with the stationary ground state of the hydrogen atom. But what is the connection between this strange *function* and the *physical state*?

This was not clear to Schrödinger either. However, after a while (in 1926) Max Born came up with a constructive suggestion. He proposed that the absolute square  $|\Psi_1(r, t)|^2$  could be interpreted as a **probability density** for the position of the electron. (Remember the corresponding interpretation in our discussion of the double-slit experiment.) Since the phase factor  $\exp(-iE_1 t/\hbar)$  is a number on the unit circle in the complex plane, the absolute value of this exponential factor is equal to 1, as stated above. (For a real number  $a$  we

have in general that  $|\exp(ia)|^2 = \exp(-ia)\exp(ia) = 1$ .) Thus the phase factor is of no importance for the probability density, which becomes **time independent**:

$$|\Psi_1(r, t)|^2 = |C_1|^2 e^{-2r/a_0}.$$

This is of course satisfactory when we are trying to describe a stationary state.

Inspired by this we shall from now on call all solutions of the Schrödinger equation on the form

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

**stationary solutions.**

(T1.30)

What does it mean to state that  $|\Psi_1|^2$  is the probability density of the position of the electron? The answer is, in analogy with the definition of for example mass density, that the probability density multiplied with a volume element  $d^3r$ ,

$$|\Psi_1(r, t)|^2 d^3r,$$

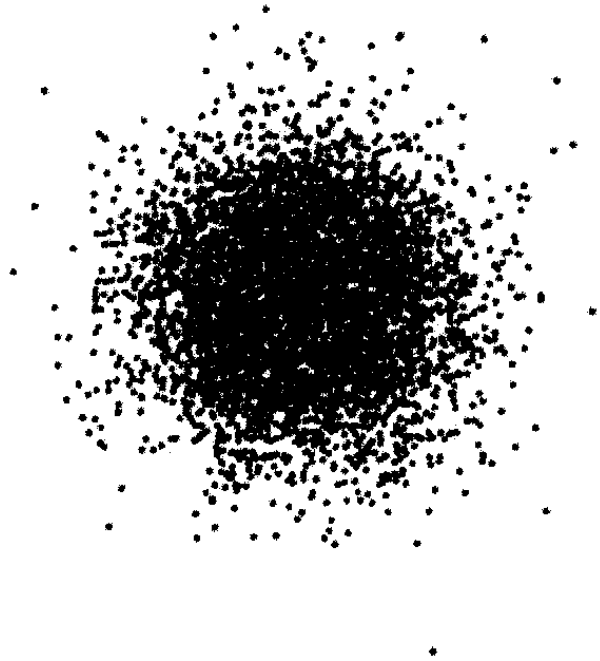
gives the probability of finding the electron within this volume element. The probability of finding the electron *somewhere* is of course equal to 1. Therefore we must require that our wave function satisfies the following **normalization condition**

$$\int |\Psi(\mathbf{r}, t)|^2 d^3r = 1 \quad (\text{normalization condition}), \quad (\text{T1.31})$$

where the integral is over the whole space. It can be shown that this condition is satisfied with  $C_1 = (\pi a_0^3)^{-1/2}$ .

To understand this a little better, let us imagine that we prepare a large number of hydrogen atoms in the state  $\Psi_1$  (the ground state), and for each of them measure the position of the electron. In analogy with the double-slit experiment, we then cannot predict the outcome of a single measurement. However, the *distribution* of the measured positions will for a large number of measurements agree well with the theoretical probability distribution

$$|\Psi_1(r, t)|^2 = |C_1|^2 e^{-2r/a_0}.$$



The results of such a series of measurements are illustrated in the figure, where each single point represents the result of one measurement. The measured positions are seen to be most densely spaced near the origin (that is, near the proton), which indeed is where the probability density  $|\Psi_1|^2$  is largest.

Both Schrödinger and Einstein disagreed strongly with Born's proposal. However, Born's strange probability interpretation of the wave function turned out to be correct. With this interpretation we can calculate e.g. the expectation value of  $r$ ,

$$\langle r \rangle \equiv \int r |\Psi_1|^2 d^3r = \dots = \frac{3}{2} a_0. \quad (\text{T1.32})$$

It is also easy to find the expectation value of  $1/r$ , which is

$$\langle 1/r \rangle \equiv \int \frac{1}{r} |\Psi_1|^2 d^3r = \frac{1}{a_0}. \quad (\text{T1.33})$$

This means that the average of the potential energy of the electron in the ground state is

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0} \langle 1/r \rangle = \dots = 2E_1 = -27.2 \text{ eV}. \quad (\text{T1.34})$$

[Show this.]

If we are asked *how big* an isolated hydrogen atom is, we now realize that it is difficult to give a definite answer, because there is for all finite distances  $r$  a non-zero probability density  $|\Psi_1|^2$ , even if this density decreases exponentially. Instead of giving a definite answer, we must therefore limit ourselves to inform about quantities like the expectation values  $\langle r \rangle = 3a_0/2$  and  $\langle 1/r \rangle^{-1} = a_0$ . Based on these results, it is reasonable to state that the Bohr Radius  $a_0 = 0.529 \times 10^{-10} \text{ m}$  is at least a *measure* of the size of the hydrogen atom (in its ground state).

For the excited states (for  $n = 2, 3, 4, \dots$ ) it turns out that the size is larger; one finds, e.g., that  $\langle 1/r \rangle^{-1} = n^2 a_0$ . So, the ground state has the lowest energy and the smallest extension. We now have an answer to the question why the atom does not shrink to the size of the proton: For the hydrogen atom, there does not exist any solution with energy lower than  $E_1 = -13.6$  eV, and with a "size" smaller than that found above, to Schrödinger's time-independent equation (T1.27).

### Some comments

(i) Based on our experience with the motion of macroscopic objects, it is natural to think that it must be possible to describe the motion of the electron around the proton in terms of a classical orbit,  $\mathbf{r} = \mathbf{r}(t)$ , which is what Bohr attempted to do. However, quantum mechanics tells us that this is in fact impossible. For phenomena on the scale of molecules, atoms and sub-atomic particles, classical mechanics simply is not valid. We do not have a classical orbit, telling us where the particle is at a given time. All we have is the information contained in the wave function for the state in question, which contains information about the probability density for the position, among other things.<sup>14</sup> The position can in principle be measured, and since the absolute square of the wave function gives the probability density, we realize that quantum mechanics is not able to predict the result of a single measurement of the position. The theory therefore has what we may call a **statistical character**. What the theory *can* predict, is the distribution of the results of a large number of measurements.

(ii) The name "wave function" can lead us to believe that  $\Psi$  describes a *physical wave*, but that is not the case. As mentioned on page 19 the "wave"  $\Psi$  is an abstract object, which must not be considered as a part of the physical system. This abstract wave exists only in our *theoretical description* of the physical system. As a reflection of this fact, the *phase* of the complex wave function can not be related to any measurable quantity; it is not measurable, in contrast to the phase of a surface wave in water, for example.

(iii) To emphasize the latter point, let us calculate the phase velocity of a de Broglie wave propagating in the  $x$  direction,

$$\Psi(x, t) = e^{i(kx - \omega t)} = e^{i(px - Et)/\hbar},$$

where  $E = p^2/2m + V$ , with  $V = \text{constant}$ . From wave theory we know that the phase velocity of this wave is  $v_f = \omega/k$ . Assuming that the potential is  $V = 0$ , we then get a phase velocity

$$v_f = \frac{\omega}{k} = \frac{E}{p} = \frac{p}{2m} = \frac{1}{2}v,$$

where  $v = p/m$  is the classical velocity of a particle with mass  $m$  and momentum  $p$ . If we suppose that  $V \neq 0$ , the result becomes even more mystical:

$$v_f = \frac{E}{p} = \frac{p^2/2m + V}{p} = \frac{1}{2}v + V/p.$$

The moral is that the phase velocity, and more generally the phase of any quantum-mechanical wave function, does not correspond to any measurable quantity, and simply has no physical meaning.

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<sup>14</sup>In chapter 2 we shall see that the wave function contains information about many things, not only the probability density for the position. We shall also learn that it is impossible to get *more* information than that contained in the wave function.

(iv) The plane de Broglie wave is defined for all  $x$  and thus has infinite extension. Therefore, it is not normalizable (to 1); the integral  $\int_{-\infty}^{\infty} |\psi(x, t)|^2 dx$  does not exist. It is not square integrable, as we say. However, this can be repaired by constructing a **wave group**. Since the time-dependent Schrödinger equation is both **linear** and **homogeneous**, the **superposition principle** is valid:

A sum of two solutions of the Schrödinger equation is also a solution.	$\left( \begin{array}{c} \text{superposition} \\ \text{principle} \end{array} \right).$	$(T1.35)$
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This holds also if the sum is replaced by an integral:

$$\Psi(x, t) = \int \phi(k) e^{i(kx - \omega t)} dk, \quad (k = p/\hbar, \omega = \hbar k^2/2m). \quad (T1.36)$$

Here,  $\phi(k)$  is a smooth distribution of wave numbers around a central value  $k_0$ . (According to de Broglie, these wave numbers correspond to momenta smoothly distributed around a central value  $p_0 = \hbar k_0$ .) From wave theory we then remember that the group velocity of this wave group  $\Psi(x, t)$  is

$$v_g = \left. \frac{d\omega}{dk} \right|_{k_0} = \frac{\hbar k_0}{m} = \frac{p_0}{m} \equiv v_0. \quad (T1.37)$$

This way we can construct a wave group that is normalizable, so that

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

(For simplicity we are here working in one dimension.) Thus the wave group is moving with precisely the velocity ( $v_0 = p_0/m$ ) which we should require for this wave group.

(v) Let us return to the ground state of the hydrogen atom. Even if this state is stationary, with a probability distribution which is time independent ("does not move"), it is important to realize that the electron is not at rest. This is because the kinetic energy is far from being equal to zero. This is understood as follows: We know that the total energy is well defined (sharp),  $E_1 = -13.6$  eV, while the expectation value of the *potential* energy is  $\langle V \rangle = -27.2$  eV. Since  $\langle K + V \rangle = \langle E \rangle = E_1$ , the expectation value of the *kinetic* energy is

$$\langle K \rangle = E_1 - \langle V \rangle = 13.6 \text{ eV}.$$

A kinetic energy of this size in fact corresponds to a velocity of the order of  $\alpha c = c/137$ . [Show this.]

## Some control questions

1. Which physical observable corresponds to the operator  $\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$  ?
2. Which operator  $\widehat{K}$  corresponds to the kinetic energy  $K = \frac{1}{2} m \mathbf{v}^2 = \mathbf{p}^2/2m$  ?
3. Show that the de Broglie wave  $\Psi_3 = \exp[i(px - p^2 t/2m)/\hbar]$  is an eigenfunction of the momentum operators  $\hat{p}_x$ ,  $\hat{p}_y$  and  $\hat{p}_z$  and of the kinetic-energy operator  $\widehat{K}$ , and determine the respective eigenvalues.
4. Same for  $\Psi_4 = \exp[i(-px - p^2 t/2m)/\hbar]$ .

5. Which physical momenta do the two de Broglie waves above correspond to?
6. Show that  $\cos kx$  is not an eigenfunction of  $\hat{p}_x$ .
7. Vis at  $\Psi_3$  oppfyller den tidsavhengige Schrödingerligningen (T1.24) for en fri partikkel.
8. Show that the real part of  $\Psi_3$  does *not* satisfy (T1.24).
9. According to the superposition principle (T1.35), the wave function  $\Psi_9 = \Psi_3 + \Psi_4$  is a solution of (T1.24), and therefore is an acceptable wave function for a free particle. Is  $\Psi_9$  an eigenfunction of the operator  $\widehat{K}$ ? Is  $\Psi_9$  an eigenfunction of  $\hat{p}_x$ ? Does  $\Psi_9$  describe a physical state with well-defined momentum?
10. At thermal equilibrium, the atoms in a one-atomic gas will (according to the so-called equipartition principle) have an average energy of  $\frac{1}{2}k_B T$  per degree of freedom, that is,  $\frac{3}{2}k_B T$  per atom. When neutrons are slowed down in a so-called moderator in a nuclear reactor, they end up as "thermal" neutrons, with an average kinetic energy  $\frac{3}{2}k_B T$ . Suppose that  $T = 300$  K and find the average kinetic energy in electron volts (eV). Calculate the de Broglie wave length of the neutron corresponding to this kinetic energy  $K$ . Do you think that the wave nature of these neutrons would be revealed by scattering them on a crystal? [Answer:  $\lambda = 1.46$  Å.]
11. When an atom is scattered by the atoms in a crystal, the scattering involves the Coulomb force between the electron and the atomic charges (electrons and nuclei). We then say that the electron experiences **electromagnetic interactions**. What kinds of interactions do you know about? Can you figure out what kind(s) of interaction are acting when neutrons are scattered on the crystal? [Remember that the neutrons are electrically neutral.]
12. Show that the function  $\psi = Ce^{ikx}$  is an eigenfunction of the momentum operator  $\hat{p}$  (see (T1.22)), and determine the eigenvalue.
13. Write down (and *memorize*) den time-dependent Schrödinger equation and the time-independent Schrödinger equation for a particle with mass  $m$  moving in a three-dimensional potential  $V(\mathbf{r})$ .
14. What is the form of these equations when the potential is one-dimensional,  $V = V(x)$ ? [Hint: The classical expression for the energy then is  $E = p_x^2/2m + V(x)$ .]

## Physical constants<sup>15</sup>

Light velocity in vacuum	$c$	$2.997\,924\,58 \cdot 10^8 \text{ m s}^{-1}$
Planck's constant	$h$	$6.626\,068\,96(33) \cdot 10^{-34} \text{ J s}$ $= 4.135\,667\,333 \cdot 10^{-15} \text{ eVs}$
Planck's constant $/(2\pi)$ ("h-strek")	$\hbar$	$1.054\,571\,628(53) \cdot 10^{-34} \text{ J s}$ $= 6.582\,118\,99(16) \cdot 10^{-16} \text{ eVs}$
Proton charge	$e$	$1.602\,176\,487(40) \cdot 10^{-19} \text{ C}$
Permittivity of vacuum	$\epsilon_0 = 1/(\mu_0 c^2)$	$8.854\,187\,817 \dots \cdot 10^{-12} \text{ F m}^{-1}$
Permeability of vacuum	$\mu_0$	$4\pi \cdot 10^{-7} \text{ N A}^{-2}$ (eksakt)

<sup>15</sup>Uncertainties in the tabulated values are given in the following way: 1.2345(13) means  $1.2345 \pm 0.0013$ .  
1 eV =  $1.602\,176\,487(40) \cdot 10^{-19} \text{ J}$ . Tabulated values from 2010.

Electron mass	$m_e$	0.510 998 910(13) MeV/ $c^2$ =9.109 382 15(45)·10 <sup>-31</sup> kg
Proton mass	$m_p$	938.272 013(23) MeV/ $c^2$ =1.672 621 637(83)·10 <sup>-27</sup> kg
Neutron mass	$m_n$	939.565 346(23) MeV/ $c^2$
Fine-structure constant	$\alpha = e^2/(4\pi\epsilon_0\hbar c)$	1/137.035 999 679(94)
Classical electron radius	$r_e = e^2/(4\pi\epsilon_0 m_e c^2)$	2.817 940 2894(58)·10 <sup>-15</sup> m
Electron Compton wavelength	$\lambda_e = h/(m_e c)$	2.426 310 2389(16)·10 <sup>-12</sup> m
Electron Compton wavelength / $(2\pi)$	$\lambda_e = \hbar/(m_e c) = r_e/\alpha$	3.861 592 6459(53)·10 <sup>-13</sup> m
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar^2/(m_e e^2)$ = $r_e/\alpha^2$	0.529 177 208 59(36)·10 <sup>-10</sup> m
Rydberg energy	$\frac{1}{2}\alpha^2 m_e c^2 = \hbar^2/(2m_e a_0^2)$	13.605 691 93(34) eV
Gravitational constant	$G_N$	6.674 28(67)·10 <sup>-11</sup> m <sup>3</sup> kg <sup>-1</sup> s <sup>-2</sup>
Avogadro's number	$N_A$	6.022 141 79(30)·10 <sup>23</sup> mol <sup>-1</sup>
Boltzmann's constant	$k_B$	1.380 6504(24)·10 <sup>-23</sup> J K <sup>-1</sup> =8.617 343(15)·10 <sup>-5</sup> eV K <sup>-1</sup>
Stefan–Boltzmann's constant	$\sigma = 2\pi^5 k_B^4/(15h^3 c^2)$	5.670 400(40)·10 <sup>-8</sup> W m <sup>-2</sup> K <sup>-4</sup>

## The greek alphabet

In quantum mechanics (and in physical literature in general) we need many more symbols than there are letters in the alphabet. Therefore it is customary to include letters from e.g. the greek alphabet. Below you will find upper-case and lower-case letters and what they are called and pronounced in Norwegian.

stor bokstav	liten bokstav	navn	uttale
A	$\alpha$	alfa	alfa
B	$\beta$	beta	beta
$\Gamma$	$\gamma$	gamma	gamma
$\Delta$	$\delta$	delta	delta
E	$\epsilon$	epsilon	epsilon
Z	$\zeta$	zeta	tseta
H	$\eta$	eta	eta
$\Theta$	$\theta$ (el. $\vartheta$ )	theta	teta
I	$\iota$	iota	iota
K	$\kappa$	kappa	kappa
$\Lambda$	$\lambda$	lambda	lambda
M	$\mu$	my	my
N	$\nu$	ny	ny
$\Xi$	$\xi$	xi	ksi
O	$\omicron$	omikron	omikron
$\Pi$	$\pi$	pi	pi
P	$\rho$	rho	ro
$\Sigma$	$\sigma$	sigma	sigma
T	$\tau$	tau	tau
$\Upsilon$	$\upsilon$	ypsilon	ypsilon
$\Phi$	$\phi$ (el. $\varphi$ )	phi	fi
X	$\chi$	khi	kji
$\Psi$	$\psi$	psi	psi
$\Omega$	$\omega$	omega	omega