Chapter 1

Wave–Particle Duality

1.1 Planck's Law of Black Body Radiation

1.1.1 Quantization of Energy

The foundation of quantum mechanics was laid in 1900 with Max Planck's discovery of the quantized nature of energy. When Planck developed his formula for black body radiation he was forced to assume that the energy exchanged between a black body and its thermal (electromagnetic) radiation is not a continuous quantity but needs to be restricted to discrete values depending on the (angular-) frequency of the radiation. Planck's formula can explain – as we shall see – all features of the black body radiation and his finding is phrased in the following way:

> **Proposition 1.1.1** *Energy is quantized and given in units of $\hbar\omega$.* $$E = \hbar\omega$$

Here ω denotes the angular frequency $\omega = 2\pi\nu$. We will drop the prefix "angular" in the following and only refer to it as the frequency. We will also bear in mind the connection to the wavelength λ given by $c = \lambda\nu$, where c is the speed of light, and to the period T given by $\nu = \frac{1}{T}$.

The fact that the energy is proportional to the frequency, rather than to the intensity of the wave – what we would expect from classical physics – is quite counterintuitive. The proportionality constant $\hbar$ is called *Planck's constant*:

$$\hbar \;=\; \frac{h}{2\pi} \;=\; 1,054 \times 10^{-34}\,\mathrm{Js} \;=\; 6,582 \times 10^{-16}\,\mathrm{eVs} \tag{1.1}$$

$$h \;=\; 6,626 \times 10^{-34}\,\mathrm{Js} \;=\; 4,136 \times 10^{-15}\,\mathrm{eVs}\,. \tag{1.2}$$

1.1.2 Black Body Radiation

A black body is by definition an object that completely absorbs all light (radiation) that falls on it. This property makes a black body a perfect source of thermal radiation. A very good realization of a black body is an oven with a small hole, see Fig. 1.1. All radiation that enters through the opening has a very small probability of leaving through it again.

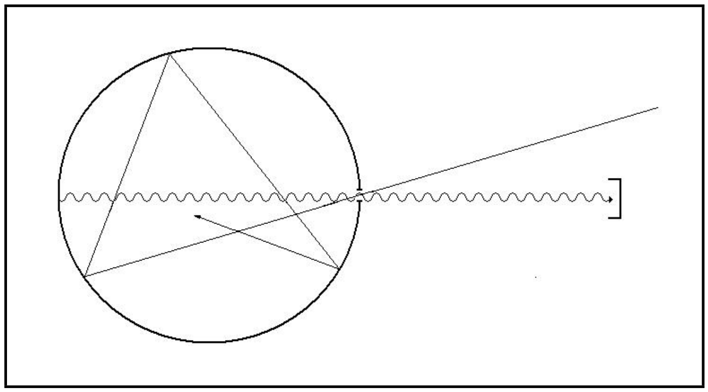

Figure 1.1: Scheme for realization of a black body as a cavity

Thus the radiation coming from the opening is just the thermal radiation, which will be measured in dependence of its frequency and the oven temperature as shown in Fig. 1.2. Such radiation sources are also referred to as (thermal) cavities.

The classical law that describes such thermal radiation is the Rayleigh-Jeans law which expresses the *energy density* $u(\omega)$ in terms of frequency ω and temperature T.

Theorem 1.1 (Rayleigh-Jeans law) $u(\omega) \;=\; \frac{kT}{\pi^2 c^3}\,\omega^2$

where k denotes *Boltzmann's constant*, $\quad k = 1,38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$.

Boltzmann's constant plays a role in classical thermo-statistics where (ideal) gases are analyzed whereas here we describe radiation. The quantity kT has the dimension of energy, e.g., in a classical system in thermal equilibrium, each degree of freedom (of motion) has a mean energy of $E = \frac{1}{2}kT$ – *Equipartition Theorem.*

From the expression of Theorem 1.1 we immediately see that the integral of the energy density over all possible frequencies is divergent,

$$\int_0^\infty d\omega \; u(\omega) \to \infty \,, \tag{1.3}$$

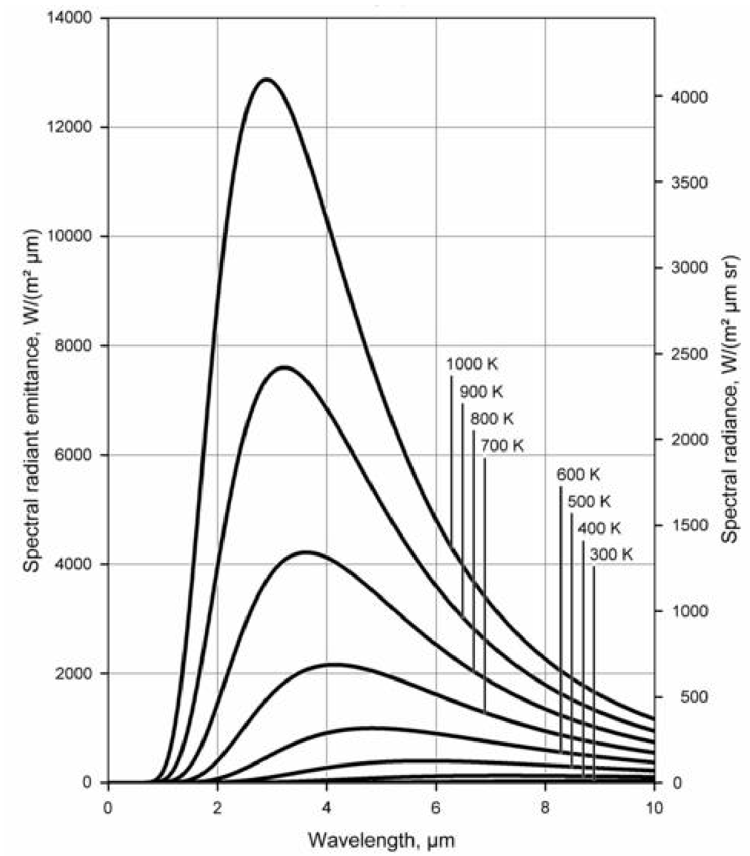

Figure 1.2: Spectrum of a black body for different temperatures, picture from: http://commons.wikimedia .org/wiki/Image:BlackbodySpectrum_lin_150dpi_en.png

which would imply an infinite amount of energy in the black body radiation. This is known as the *ultraviolet catastrophe* and the law is therefore only valid for small frequencies.

For high frequencies a law was found empirically by Wilhelm Wien in 1896.

Theorem 1.2 (Wien's law) $u(\omega) \rightarrow A\,\omega^3 e^{-B\frac{\omega}{T}} \quad \textit{for} \quad \omega \rightarrow \infty$

where A and B are constants which we will specify later on.

As already mentioned Max Planck derived an impressive formula which interpolates[1] between the Rayleigh-Jeans law and Wien's law. For the derivation the correctness of Proposition 1.1.1 was necessary, i.e., the energy can only occur in quanta of $\hbar\omega$. For this achievement he was awarded the 1919 nobel prize in physics.

[1]See Fig. 1.3

Theorem 1.3 (Planck's law) $$u(\omega) \;=\; \frac{\hbar}{\pi^2 c^3} \, \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1}$$

From Planck's law we arrive at the already well-known laws of Rayleigh-Jeans and Wien by taking the limits for $\omega \to 0$ or $\omega \to \infty$ respectively:

$$\begin{array}{lcl} \text{for} \;\; \omega \to 0 & & \to \;\; \text{Rayleigh-Jeans} \\ & u(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1} & \\ \text{for} \;\; \omega \to \infty & & \to \;\; \text{Wien} \end{array}$$

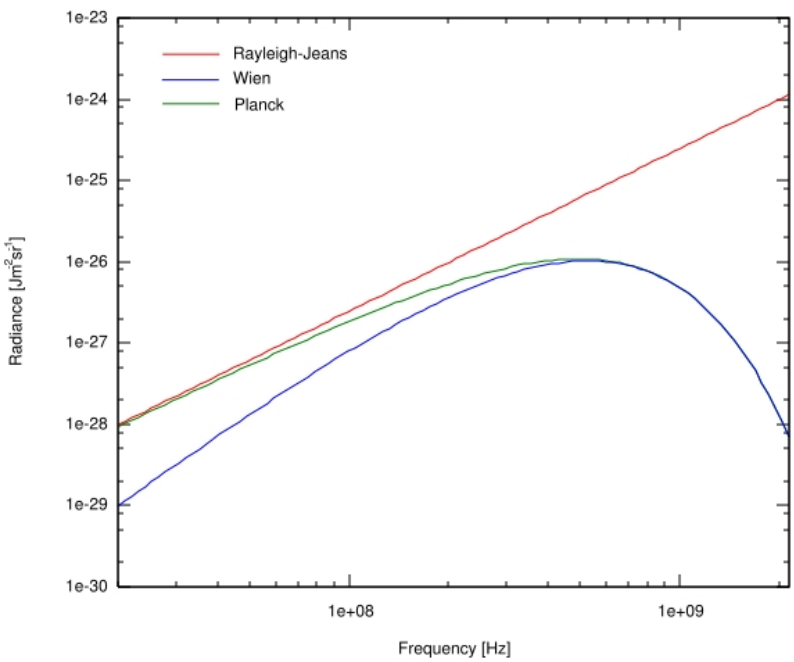

Figure 1.3: Comparison of the radiation laws of Planck, Wien and Rayleigh-Jeans, picture from: http://en.wikipedia.org/wiki/Image:RWP-comparison.svg

We also want to point out some of the consequences of Theorem 1.3.

- **Wien's displacement law**: $\boxed{\lambda_{\text{max}} T \;=\; const. \;=\; 0,29\,\text{cm K}}$
- **Stefan-Boltzmann law**: for the radiative power we have

$$\int_0^\infty d\omega \, u(\omega) \;\propto\; T^4 \int_0^\infty d\left(\frac{\hbar\omega}{kT}\right) \frac{\left(\frac{\hbar\omega}{kT}\right)^3}{\exp\left(\frac{\hbar\omega}{kT}\right) \,-\, 1} \tag{1.4}$$

substituting $\frac{\hbar\omega}{kT} = x$ and using formula

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15} \tag{1.4}$$

we find the proportionality $\boxed{\propto T^4}$

1.1.3 Derivation of Planck's Law

Now we want to derive Planck's law by considering a black body realized by a hollow metal ball. We assume the metal to be composed of two energy-level atoms such that they can emit or absorb photons with energy $E = \hbar\omega$ as sketched in Fig. 1.4.

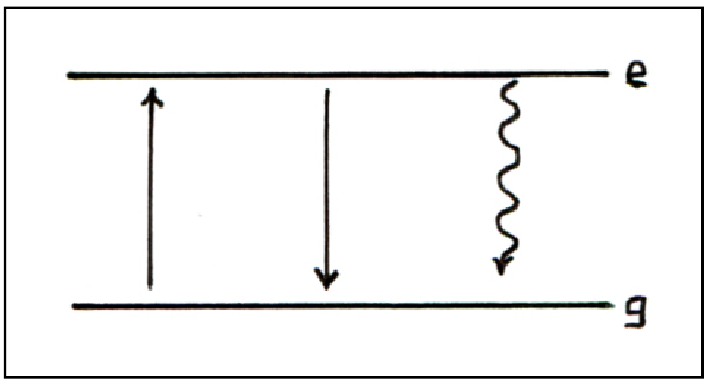

Figure 1.4: Energy states in a two level atom, e... excited state, g... ground state. There are three processes: absorption, stimulated emission and spontaneous emission of photons.

Further assuming thermal equilibrium, the number of atoms in ground and excited states is determined by the (classical) *Boltzmann distribution* of statistical mechanics

$$\frac{N_e}{N_g} = \exp\left(-\frac{E}{kT}\right), \tag{1.5}$$

where $N_{e/g}$ is the number of excited/non-excited atoms and T is the thermodynamical temperature of the system.

As Einstein first pointed out there are three processes: the absorption of photons, the stimulated emission and the spontaneous emission of photons from the excited state of the atom, see Fig. 1.4. The stimulated processes are proportional to the number of photons whereas the spontaneous process is not, it is just proportional to the transition rate. Furthermore, the coefficients of absorption and stimulated emission are assumed to equal and proportional to the probability of spontaneous emission.

Now, in the thermal equilibrium the rates for emission and absorption of a photon must be equal and thus we can conclude that:

Absorption rate:	$N_g\,\overline{n}\,P$	P ... probability for transition
Emission rate:	$N_e\,(\overline{n}+1)\,P$	$\overline{n}$ ... average number of photons

$$\Rightarrow$$

$$N_g\,\overline{n}\,P \;=\; N_e\,(\overline{n}+1)\,P \quad\Rightarrow\quad \frac{\overline{n}}{\overline{n}+1} \;=\; \frac{N_e}{N_g} \;=\; \exp\left(-\frac{E}{kT}\right) \;=\; \exp\left(-\frac{\hbar\omega}{kT}\right)$$

providing the average number of photons in the cavern[2]

$$\overline{n} \;=\; \frac{1}{e^{\frac{\hbar\omega}{kT}}-1}\,, \tag{1.6}$$

and the average photon energy

$$\overline{n}\,\hbar\omega \;=\; \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}}-1}\,. \tag{1.7}$$

Turning next to the energy density we need to consider the photons as standing waves inside the hollow ball due to the periodic boundary conditions imposed on the system by the cavern walls. We are interested in the number of possible modes of the electromagnetic field inside an infinitesimal element dk, where $k = \frac{2\pi}{\lambda} = \frac{\omega}{c}$ is the wave number.

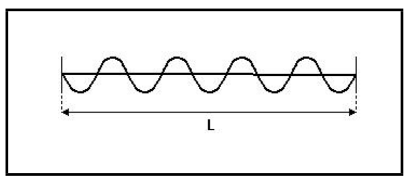

Figure 1.5: Photon described as standing wave in a cavern of length L.

The number of knots N (wavelengths) of this standing wave is then given by

$$N \;=\; \frac{L}{\lambda} \;=\; \frac{L}{2\pi}\frac{2\pi}{\lambda} \;=\; \frac{L}{2\pi}k\,, \tag{1.8}$$

which gives within an infinitesimal element

$$\text{1-dim:}\quad dN \;=\; \frac{L}{2\pi}dk \qquad \text{3-dim:}\quad dN \;=\; 2\,\frac{V}{(2\pi)^3}d^3k\,, \tag{1.9}$$

where we inserted in 3 dimensions a factor 2 for the two (polarization) degrees of freedom of the photon and wrote L^3 as V, the volume of the cell. Furthermore, inserting $d^3k = 4\pi k^2 dk$ and using the relation $k = \frac{\omega}{c}$ for the wave number we get

$$dN \;=\; 2\,\frac{V}{(2\pi)^3}\frac{4\pi\omega^2 d\omega}{c^3}\,. \tag{1.10}$$

We will now calculate the energy density of the photons.

[2]Note that in our derivation P corresponds to the Einstein coefficient A and $\overline{n}\,P$ to the Einstein coefficient B in Quantum Optics.

1. **Classically:** In the classical case we follow the *equipartition theorem*, telling us that in thermal equilibrium each degree of freedom contributes $E = \frac{1}{2}kT$ to the total energy of the system, though, as we shall encounter, it does not hold true for quantum mechanical systems, especially for low temperatures.

   Considering the standing wave as harmonic oscillator has the following mean energy:

   $$E \;=\; \langle E_{\text{kin}} \rangle + \langle V \rangle \;=\; \left\langle \frac{m}{2} v^2 \right\rangle + \left\langle \frac{m\omega}{2} x^2 \right\rangle \;=\; \frac{1}{2} kT + \frac{1}{2} kT \;=\; kT \,. \tag{1.11}$$

   For the oscillator the mean kinetic and potential energy are equal[3], $\langle E_{\text{kin}} \rangle = \langle V \rangle$, and both are proportional to quadratic variables which is the equipartition theorem's criterion for a degree of freedom to contribute $\frac{1}{2}kT$. We thus can write $dE = kT\,dN$ and by taking equation (1.10) we calculate the (spectral) energy density

   $$u(\omega) \;=\; \frac{1}{V}\frac{dE}{d\omega} \;=\; \frac{kT}{\pi^2 c^3}\,\omega^2 \,, \tag{1.12}$$

   which we recognize as Theorem 1.1, the Rayleigh-Jeans Law.

2. **Quantum-mechanically:** In the quantum case we use the average photon energy, equation (1.7), we calculated above by using the quantization hypothesis, Proposition 1.1.1, to write $dE = \overline{n}\,\hbar\omega\,dN$ and again inserting equation (1.10) we calculate

   $$u(\omega) \;=\; \frac{1}{V}\frac{dE}{d\omega} \;=\; \frac{\hbar}{\pi^2 c^3}\,\frac{\omega^3}{e^{\frac{\hbar\omega}{kT}} - 1} \,, \tag{1.13}$$

   and we recover Theorem 1.3, Planck's Law for black body radiation.

1.2 The Photoelectric Effect

1.2.1 Facts about the Photoelectric Effect

In 1887 Heinrich Hertz discovered a phenomenon, the photoelectric effect, that touches the foundation of quantum mechanics. A metal surface emits electrons when illuminated by ultraviolet light. The importance of this discovery lies within the inability of classical physics to describe the effect in its full extent based on three observations.

1.) The kinetic energy of the emitted electrons is independent of the intensity of the illuminating source of light and

2.) increases with increasing frequency of the light.

3.) There exists a threshold frequency below which no electrons are emitted.

[3] This statement results from the so-called Virial theorem, stating that $\langle 2E_{\text{kin}} \rangle = \left\langle x\frac{dV}{dx} \right\rangle$, which we will encounter later on in Section 2.7.

More accurate measurements were made by Philipp Lenard between 1900 and 1902 for which he received the nobel prize in 1905.

In terms of classical physics this effect was not understood as from classical electrodynamics was known that the

$$\text{energy density:} \quad u = \frac{1}{8\pi}\left(\vec{E}^2 + \vec{B}^2\right) \tag{1.14}$$

$$\text{and the} \quad \text{energy flux:} \quad S = \frac{c}{8\pi}\,\vec{E}\times\vec{B} \tag{1.15}$$

are both proportional to the intensity. Thus "knocking" electrons out of the metal is possible, but there is no threshold that limits this process to certain frequencies. As long as the surface is exposed to the radiation the electrons absorb energy until they get detached from the metal.

1.2.2 Einstein's Explanation for the Photoelectric Effect

The phenomenon of the photoelectric effect could then be explained by Albert Einstein in 1905 with his photon hypothesis which he was also awarded the nobel prize for in 1921.

> **Proposition 1.2.1 (Photon hypothesis)**
> *Light consists of quanta (photons) with respective energy of $E = \hbar\omega$ each.*

Einstein explained the effect in the following way. The incident photons transfer their energy to the electrons of the metal. Since the electrons are bound to the metal the energy need to be sufficient to overcome the electrostatic barrier of the metal. The respective energy, which is dependent on the material used is termed the work function of the material.

> **Proposition 1.2.2 (Photoelectric formula)** $E_{\text{kin}} = \frac{mv^2}{2} = \hbar\omega - W$

where W is the *work function* of the metal. From Proposition 1.2.2 we understand that the kinetic energy of the emitted electrons is bounded by the frequency of the incident light such that $E_{\text{kin,e}^-} < \hbar\omega_{\text{photon}}$ and we conclude that a threshold frequency ω_0 must exist where the emitted electrons are at rest $E_{\text{kin,e}^-} = 0$ after escaping the potential of the metal.

$$\text{Threshold frequency} \quad \boxed{\omega_0 = \frac{W}{\hbar}}$$

For frequencies $\omega < \omega_0$ no electrons are emitted and we have reflection or scattering of the incident light together with electronic and/or thermal excitation instead. Einstein's explanation caused serious debates amongst the community and was not generally accepted due to conceptual difficulties to unify the quantized (particle) nature of light with Maxwell's equations, which stood on solid ground experimentally, suggesting a wave-like behaviour of light. The experiment to change that point of view was performed by Robert Andrews Millikan.

1.2.3 The Millikan Experiment

In 1916 R.A.Millikan developed an experimental setup (sketched in Fig. 1.6) which allowed to check the accuracy of Einstein's formula (Proposition 1.2.2). He was awarded the Nobel prize for his work on the electron charge and the photoelectric effect in 1923.

A photocathode is irradiated with ultraviolet light which causes the emission of electrons thus generating an electric current, between the cathode and the electron collector, that is measured by a galvanometer. Additionally a voltage is installed such that the electrons are hindered in advancing the collector. The electrons now need to raise energy, respective to the voltage U, to get to the collector and generate the current. So if $eU > E_{\text{kin}}$ no electrons arrive at the collector. If however the voltage is regulated to a value U_0 such that the current (as measured by the galvanometer) tends to zero, then U_0 is a measure for the kinetic energy. This allows us to measure the work function of the metal at hand[4].

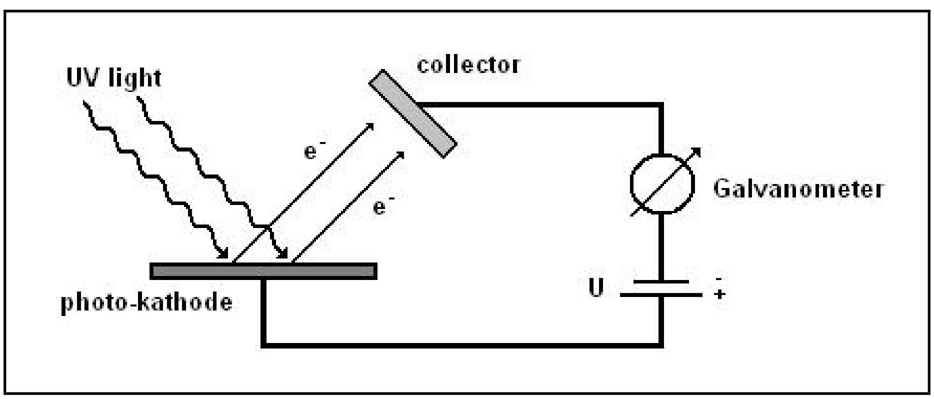

Figure 1.6: Schematic overview of the Millikan experiment

$$\boxed{eU_0 = E_{\text{kin}} = \hbar\omega - W} \quad \rightarrow \text{ work function } W \ (\approx 2{-}5 \text{ eV for typical metals})$$

Furthermore, the set up allows for a precise measurement of Planck's constant as can be seen in Fig. 1.7.

[4] assuming the collector and emitter are of the same material, otherwise an additional contact voltage needs to be considered

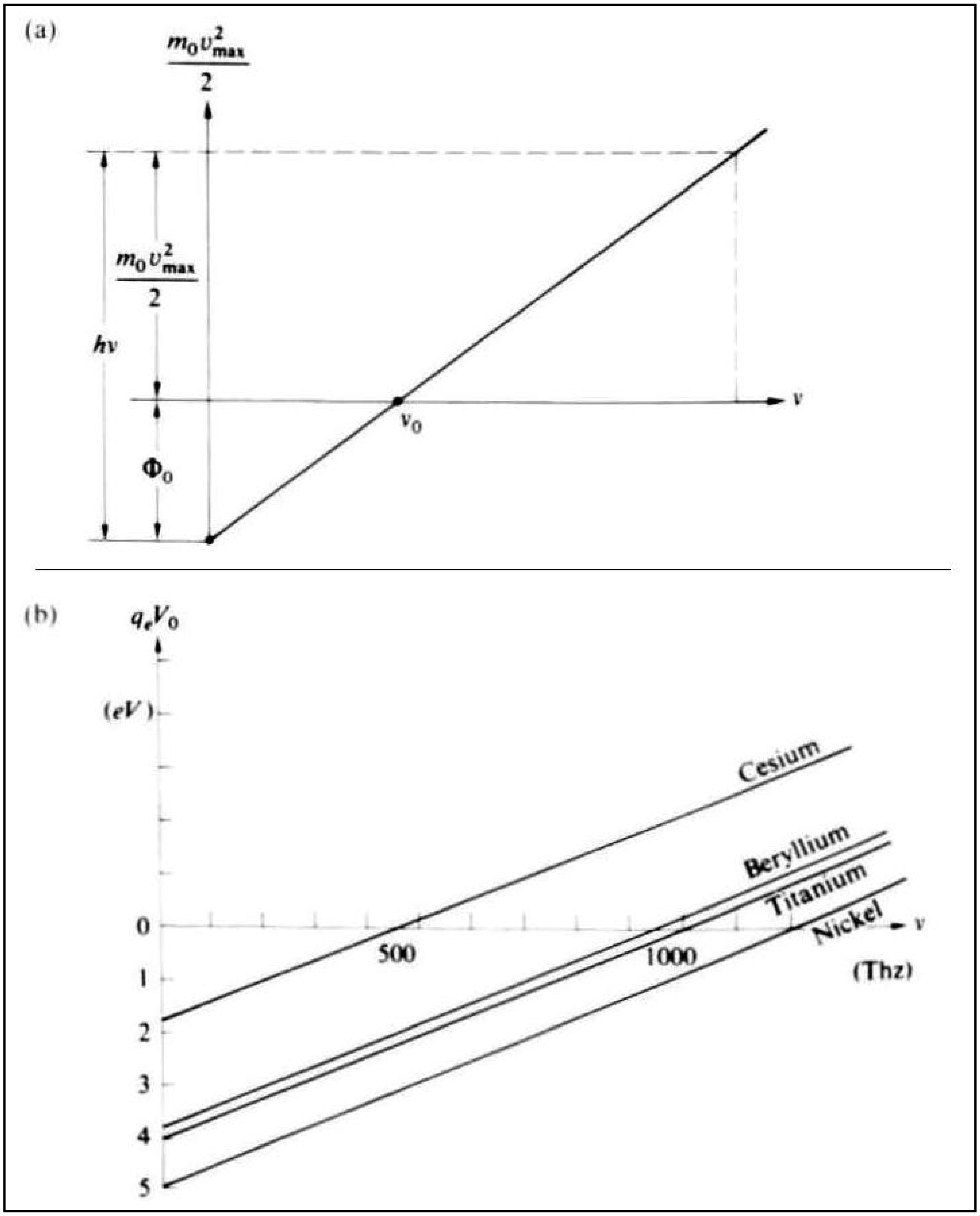

Figure 1.7: Determination of Planck's constant: a) Measuring the kinetic energy of the electrons as a function of the incident radiation frequency, gives Planck's constant as the slope of the resulting linear function. b) Results are shown for different materials displaying the workfunctions as the respective vertical intercepts; pictures from [2]

With the confirmation of Einstein's formula we now want to take a look at the properties of the thus introduced photons. From special relativity we know that energy and velocity are related by

$$1)\quad E = \sqrt{p^2c^2 + m^2c^4} \quad \text{and} \quad 2)\quad \vec{v} = \frac{\partial E}{\partial \vec{p}} = \frac{\vec{p}c^2}{\sqrt{p^2c^2 + m^2c^4}}\,, \tag{1.16}$$

since for the photon the velocity is $|\vec{v}| = c \cong 2,99.10^{10}\mathrm{cms}^{-1}$ we conclude $\Rightarrow$ $\boxed{m_{\text{photon}} = 0}$
The photon is massless.

If we then compare the energy of the photon as given by special relativity $E = pc$ and quantum mechanics $E = \hbar\omega$ we get the momentum of the photon:

$$k = \frac{\omega}{c} \quad \Rightarrow \quad E = \hbar kc \quad \Rightarrow \quad p = \hbar k\,.$$

$$\text{Momentum of the photon} \qquad \boxed{\vec{p}_{\text{photon}} = \hbar\vec{k}}$$

1.3 The Compton Effect

Another effect that revealed the quantized nature of radiation was the (elastic) scattering of light on particles, called Compton effect or Compton scattering, see Fig. 1.8. For a description we study energy and momentum of the photon, both particle properties. The effect works in total analogy to a scattering process with particles, i.e. energy and momentum are conserved.

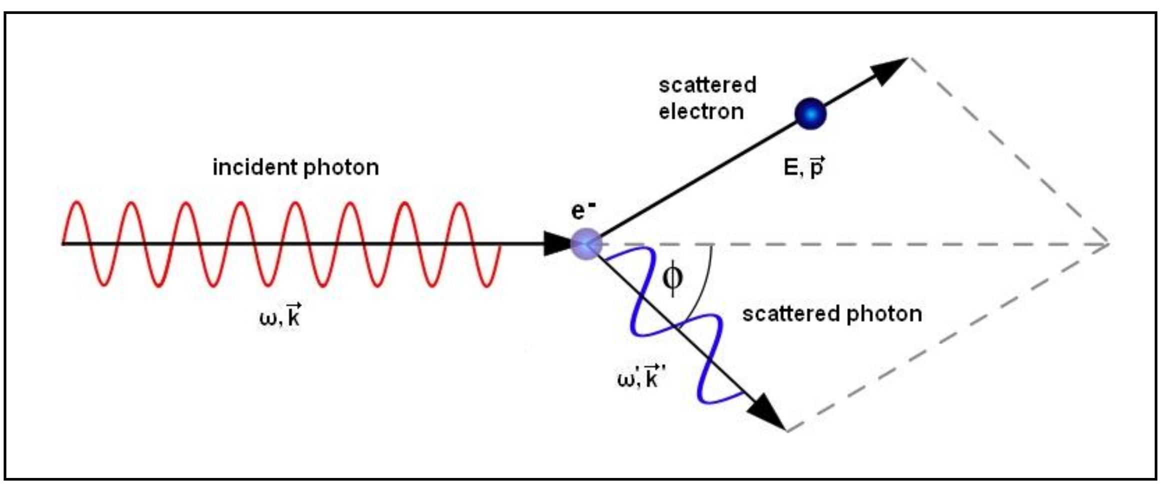

Figure 1.8: Compton effect: scattering of a photon on a resting electron, picture from: http://de.wikipedia.org/wiki/Bild:Compton_scattering-de.svg

1.3.1 The Compton Shift Formula

We assume:

conservation of energy:

$$\hbar\omega + mc^2 = \hbar\omega' + E\,, \tag{1.17}$$

conservation of momentum:

$$\hbar\vec{k} = \hbar\vec{k}' + \vec{p}\,. \tag{1.18}$$

From Eqs. (1.17) and (1.18) we find the following relation when using the relativistic energy $E^2 = p^2c^2 + m^2c^4$, Eq. (1.16), for the electron

$$\frac{1}{c^2}\left(\hbar\omega - \hbar\omega' + mc^2\right)^2 \;-\; \hbar^2\left(\vec{k} - \vec{k}'\right)^2 \;=\; \frac{1}{c^2}E^2 - \vec{p}^{\,2} \;=\; m^2c^2\,. \tag{1.19}$$

Recalling that $\omega = kc$, $\omega' = k'c$, $k = |\vec{k}|$ and $\vec{k}\vec{k}' = kk'\cos\phi$ we calculate

$$\begin{aligned}
\frac{1}{c^2}\hbar^2\left(\omega - \omega'\right)^2 \quad &= \hbar^2\left(k - k'\right)^2 \quad = \quad \hbar^2\left(k^2 + k'^2 - 2kk'\right)\\
\text{and} \quad -\,\hbar^2\left(\vec{k} - \vec{k}'\right)^2 \quad &= -\,\hbar^2\left(k^2 + k'^2 - 2\vec{k}\vec{k}'\right) = -\,\hbar^2\left(k^2 + k'^2 - 2kk'\cos\phi\right)
\end{aligned}$$

which we insert into Eq. (1.19) and obtain

$$\begin{aligned}
m^2c^2 + 2mc\hbar\left(k - k'\right) \;\; - \;\; 2\hbar^2 kk'\left(1 - \cos\phi\right) \;\; &= \;\; m^2c^2\\
k - k' \;\; &= \;\; \frac{\hbar}{mc}kk'\left(1 - \cos\phi\right)\\
2\pi\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right) \;\; &= \;\; \frac{\hbar}{mc}\frac{(2\pi)^2}{\lambda\lambda'}2\sin^2\frac{\phi}{2}\;.
\end{aligned}$$

Multiplying finally both sides by $\frac{\lambda\lambda'}{2\pi}$ and denoting $\lambda' - \lambda = \Delta\lambda$, we arrive at the formula:

Lemma 1.1 (Compton shift formula) $\Delta\lambda \;=\; \lambda' - \lambda \;=\; 4\pi\frac{\hbar}{mc}\,\sin^2\frac{\phi}{2}$

Result: We discover that the wavelength of the scattered photon has increased (or the frequency has decreased) relatively to the incoming photon due to the energy transfer to the electron. The difference $\Delta\lambda$ is directly related to the *scattering angle* ϕ.

It is customary to define the *Compton wavelength* $\lambda_{\mathrm{c}} = \frac{h}{mc}$ ($= 2,43 \times 10^{-10}$ cm for electrons).

Since λ_c is very small, high energy radiation (X-rays) is needed to observe the effect. If we choose a wavelength of 7×10^{-9} cm for the X-rays we estimate for a maximal scattering angle an effect of

$$\frac{\Delta\lambda}{\lambda} = \frac{2\lambda_c}{\lambda_{\text{Xray}}} = \frac{2 \times 2,43 \times 10^{-10}\text{cm}}{7 \times 10^{-9}\text{cm}} \approx 0,07 = 7\,\%\,. \tag{1.20}$$

1.3.2 The Experiment of Compton

In the experiment by A.H.Compton, which he received the Nobel prize for in 1927, X-rays are scattered by nearly free electrons in carbon (graphite) as seen in Fig. 1.9. The intensity of the outgoing radiation is then measured as a function of its wavelength as can be seen in Fig. 1.10.

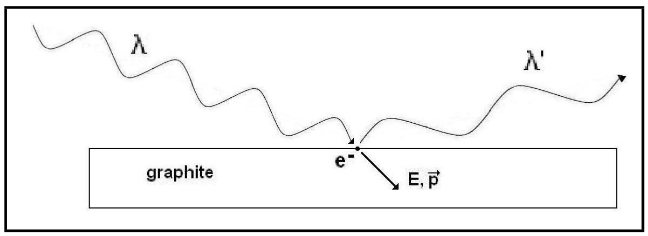

Figure 1.9: Experiment of Compton: scattering of X-rays by electrons in the surface of a carbon block

The intensity of the scattered peak (due to the quasi-free electrons in the material) increases at the expense of the unscattered peak which remains (due to electrons bound to the atom that do not allow a shift in the energy or wavelength). In fact, we have $I^{\text{max}}_{scattered} > I^{\text{max}}_{unscattered}$.

Résumé: The particle character of light is confirmed in Compton's experiment and we assign the energy of $E = \hbar\omega$ and the momentum $\vec{p} = \hbar\vec{k}$ to the (undivisible) photon. The Compton formula (Lemma 1.1) reveals a proportionality to $\hbar$, a quantum mechanical property, which is confirmed in the experiment. Classically no change of the wavelength is to be expected.

1.4 Bohr's Theses

In the early nineteenhundreds many elementary questions about our understanding of matter, especially atoms, and radiation were unanswered and created serious problems. E.g.: Why don't electrons tumble into the atomic nucleus? If the electrons rotate around the nucleus, they would be in accelerated motion thus radiating, i.e., losing their energy which keeps them on their paths. Another important question was why are sharp spectral lines observed. In an attempt to overcome those issues Niels Bohr postulated new rules incompatible with classical notions, which were quite revolutionary at that time.

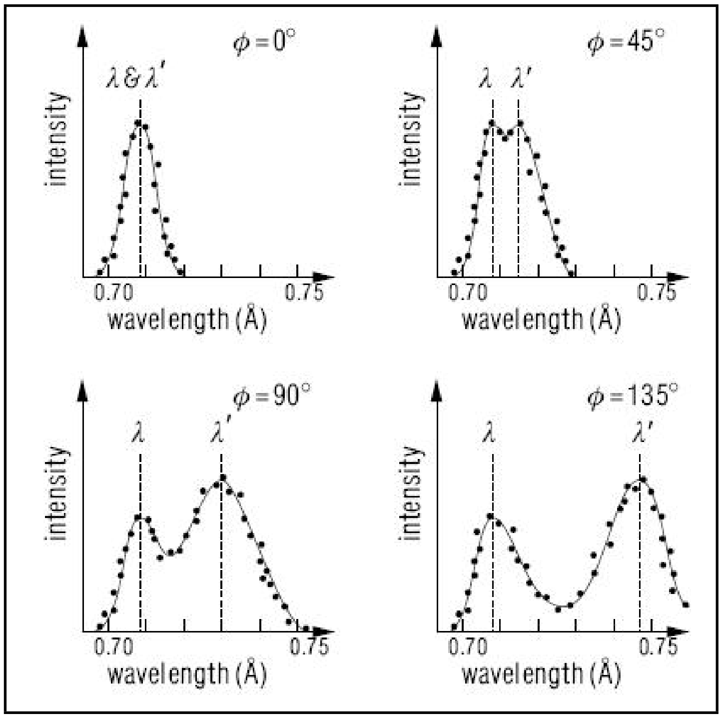

Figure 1.10: Compton shift: intensity of radiation as detected after the scattering process, the scattered line is shifted against the remaining unscatterd line by $\Delta\lambda$ depending on the scattering angle ϕ, picture from Ref. [1]

Proposition 1.4.1 (Bohr's quantum postulate)
Electrons can only take certain discrete energy values in the atom. During the transition from a state with energy E_{n} to another state with energy E_{m} a photon with frequency $\omega = \frac{1}{\hbar}|\,(E_{\mathrm{n}} - E_{\mathrm{m}})\,|$ is emitted ($E_{\mathrm{n}} > E_{\mathrm{m}}$) or absorbed ($E_{\mathrm{n}} < E_{\mathrm{m}}$).

Bohr's atom model: Having postulated the correspondence between energy levels and the emitted/absorbed photons the next step was to postulate how these energy levels came to be.

Proposition 1.4.2 (Bohr's quantization rule)
States are stationary if their respective classical paths are quantized such that their action functional obeys

$$\oint p\, dq = nh$$

where n is an integer number ($n = 1, 2, ...$).

The energy spectrum for the hydrogen atom, given by the *Rydberg-formula* and empirically already known before Bohr's proposition, was then explained in Bohr's theory as the energy of an electron transition between two orbitals n and m. Furthermore Bohr's model could theoretically predict the value of the Rydberg constant R

$$\hbar\omega \;=\; E_{\mathrm{n}} - E_{\mathrm{m}} \;=\; R\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \quad \text{or} \quad \frac{1}{\lambda} \;=\; \frac{R}{hc}\left(\frac{1}{m^2} - \frac{1}{n^2}\right)\,, \tag{1.21}$$

where $\frac{R}{hc} \;=\; \frac{2\pi^2 m\, e^4}{h^3 c} \;=\; 1,097 \times 10^5\,\mathrm{cm}^{-1}$ is the *Rydberg constant.*

Although the model of Bohr allows a very simple and intuitive visualization, electrons orbiting on fixed paths around the nucleus, creating an analogue to planetary movement[5], it turns out the model is not only too simple but just wrong. Nevertheless Bohr's model represented a great step forward but it was clear that this *ad hoc* prescriptions couldn't be considered as a definitive theory. In fact, as it turned out, the perception of particles following distinct paths altogether has no meaning for quantum mechanical calculations and only certain interpretations of quantum mechanics allow for their existence at all. But generally, as we shall see in Sect. 1.7, we need to cast aside the concept of a trajectory in quantum mechanics.

Another issue that arose was the debate whether light was a wave or composed of particles, concepts which seemed to contradict each other but were both observed under certain conditions. Bohr tried to formulate this problem in the following way:

Proposition 1.4.3 (Bohr's complementarity principle)
Wave and particle are two aspects of describing physical phenomena, which are complementary to each other.

Depending on the measuring instrument used, either waves or particles are observed, but never both at the same time, i.e. wave- and particle-nature are not simultaneously observable.

Similar statements can be made about other *complementary quantities* like position and momentum, energy and time, spin in orthogonal directions (e.g.: σ_{x} and σ_{y}).

Some of these questions are still subject of interest and play important roles in experiments regarding "which way detectors", "quantum erasers" and "continuous complementarity" to name but a few.

[5]Arnold Sommerfeld, 1868 – 1951, a prominent physicists at that time and teacher of many Nobel prize winners like Heisenberg, Pauli and Bethe, has extended Bohr's atom model to explain the fine structure of hydrogen.

A question remaining, which still causes discussion, is the connection of quantum mechanics to classical physics which Bohr phrased as such:

Proposition 1.4.4 (Bohr's correspondence principle)
In the limit of large quantum numbers classical physics is reproduced.

The propositions of this section form the basis for what is usually referred to as the *Copenhagen interpretation of quantum mechanics*, which was developed mainly by Niels Bohr and Werner Heisenberg.

Bohr was *the* leading figure of quantum physics at that time and his institute in Copenhagen became the center of the avantgarde of physics where physicists all over the world met, just to mention some names: Heisenberg, Pauli, Gamow, Landau, Schrödinger, Kramers, ... Bohr's dispute with Einstein about the foundations of quantum mechanics became legendary. Bohr was awarded the Nobel prize in 1922.

1.5 Wave Properties of Matter

As we will see in this section, not only radiation, but also massive particles are in need of a more sophisticated description than given by classical mechanics. To associate microscopical (quantum) objects, as for example electrons, with idealized (especially localized) point-particles, carrying sharp momenta, is not only misleading, but simply wrong (see Sect. 1.6 and Sect. 2.6) and can not account for all observed phenomena. A very important step towards a more complete description was Louis de Broglie's proposal of wavelike behaviour of matter in 1923, which he received the Nobel prize for in 1929.

1.5.1 Louis de Broglie's Hypothesis

In view of particle properties for light waves – photons – Louis de Broglie ventured to consider the reverse phenomenon, he proposed to assign wave properties to matter, which we will formulate here in the following way:

Proposition 1.5.1 (Louis de Broglie's hypothesis)
To every particle with mass m, momentum $\vec{p}$ and energy E a wavelength of $\lambda_{\text{deBroglie}} = \frac{h}{|\vec{p}|} = \frac{h}{\sqrt{2mE}}$ is associated, where $E = E_{\text{kin}} = \frac{\vec{p}^{\,2}}{2m}$.

The above statement can be easily understood when assigning energy and momentum

$$E = \hbar\omega \quad \text{and} \quad p = \hbar k = \frac{h}{\lambda} \tag{1.22}$$

to matter in (reversed) analogy to photons. If we then express the wavelength λ through the momentum p and use the form of the kinetic energy $E = p^2/2m$ to write $p = \sqrt{2mE}$ we directly get the *de Broglie wavelength* $\lambda_{\mathrm{deBroglie}}$ of massive particles.

In this connection the notion of *matter waves* was introduced. De Broglie's view was that there exists a *pilot wave* which leads the particle on definite trajectories. This point of view – wave *and* particle – being in contrast to Bohr's view leads, however, into serious difficulties as we shall see.

Note that above wave assignment was made for free particles, i.e. particles that are not subjected to any outer potential. The question whether the potential energy would influence his hypothesis was also raised by de Broglie and will be tangible when we consider Schrödinger's theory (see Chapt. 2) where also the nature of the waves becomes more evident in terms of Max Born's probability interpretation (see Sect. 1.7).

1.5.2 Electron Diffraction from a Crystal

To test his hypothesis de Broglie proposed an experiment with electrons. He observed that, following Proposition 1.5.1, electrons with a kinetic energy of several eV and mass $m_{\mathrm{e}} = 0,5\,\mathrm{MeV}$ would have a de Broglie wavelength of a few $\mathring{A}$. For example, for an energy of $10\,\mathrm{eV}$ we obtain $\lambda_{\mathrm{deBroglie}} = 3,9\ \mathring{A}$, which is the same order of magnitude as the lattice spacing of atoms in crystals, thus making it possible to diffract electrons from the lattice analogously to the diffraction of light from a grating.

The corresponding experiment has been performed by C.Davisson and L.Germer in 1927 and independently by G.P. Thomson. It involved electrons which were sent with appropriate velocity onto a nickel crystal with lattice spacing $d \cong 0,92\ \mathring{A}$, see Fig. 1.11.

The intensity of the outgoing electron beam was then measured for different angles, reproducing the diffraction pattern postulated by W.H.Bragg and (his son) W.L.Bragg for X-rays. The similarity of X-ray- and electron-diffraction can be seen in Fig. 1.12.

The Bragg condition for constructive interference is $\boxed{\sin\theta = \frac{n\lambda}{2d}}\,,\ \ n \in N\,.$

The observation of an intensity maximum of the diffraction (Bragg peak) for a scattering angle $\varphi = 50°$, which translates to the angle in the Bragg condition of $\Theta = 65°$, gives us

$$\Rightarrow \quad \lambda \;=\; 2 \times 0,92\ \mathring{A} \times \sin 65° \;=\; 1,67\ \mathring{A}\,,$$

which is in perfect accordance with the de Broglie wavelength for an acceleration voltage of $U = 54\,\mathrm{V}$ used in this experiment.

The Davisson-Germer experiment thus helped to confirm the wavelike nature of matter

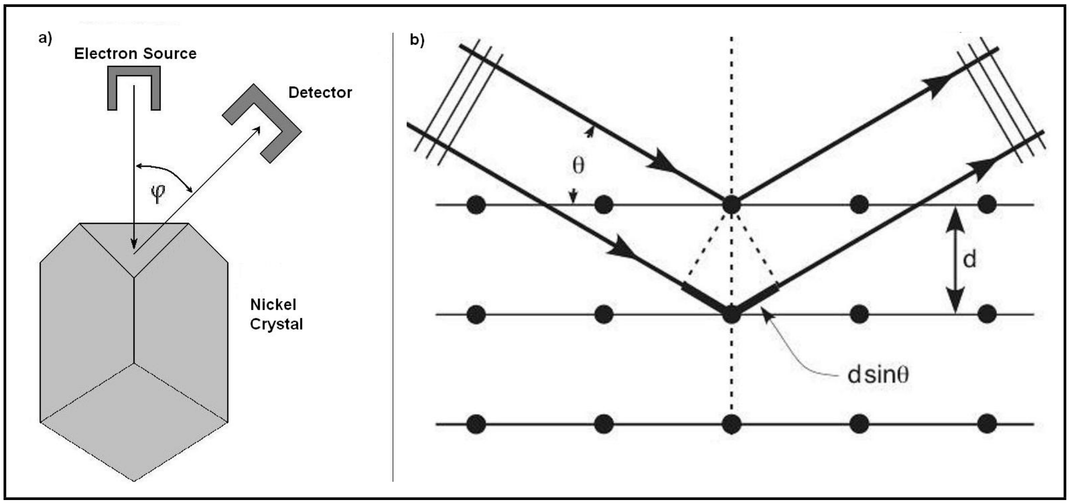

Figure 1.11: Davisson-Germer Experiment: a) An electron beam is diffracted from a nickel crystal and the intensity of the outgoing beam is measured. b) Scheme of the Bragg diffraction from a crystal with lattice spacing d, picture (b) from: http://en.wikipedia.org/wiki/Image:Bragg_diffraction.png

and to validate the claims of early quantum mechanics. Davisson and Thomson[6] were awarded the Nobel prize in 1937.

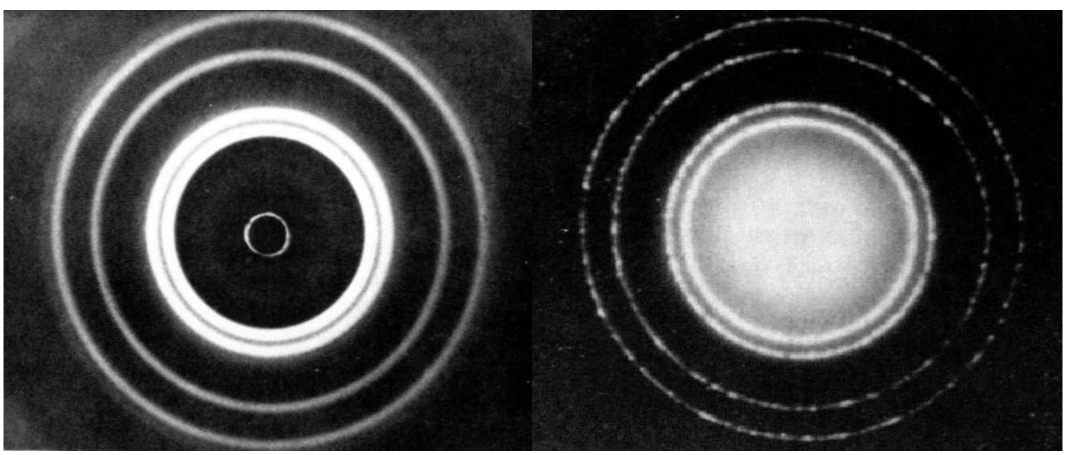

Figure 1.12: Comparison of X-ray- (left) and electron- (right) diffraction patterns caused by the same aperture, namely a small hole in an aluminium foil; pictures from Ref. [2]

[6]It's quite amusing that his father J.J. Thomson received the Nobel prize in 1906 for showing the "opposite", namely that the electron is a particle.

1.6 Heisenberg's Uncertainty Principle

We now want to introduce a quantum mechanical principle, *Heisenberg's uncertainty principle* that is somehow difficult to grasp conceptually even though the mathematics behind is straightforward. Before we will derive it formally, which we will do in Sect. 2.6, we try to make it plausible by more heuristic means, namely by the *Heisenberg microscope*. The Gedankenexperiment of the Heisenberg microscope needs to be seen more as an example for the application of the uncertainty principle, than a justification of the principle itself.

1.6.1 Heisenberg's Microscope

Let's start by detecting the position of an electron by scattering of light and picturing it on a screen. The electron will then appear as the central dot (intensity maximum) on the screen, surrounded by bright and dark concentric rings (higher order intensity maxima/minima). Since the electron acts as a light source we have to consider it as an aperture with width d where we know that the condition for destructive interference is

$$\sin\phi \;=\; \frac{n\lambda}{d} \;\;,\; n \in \mathbb{N}\,. \tag{1.23}$$

So following Eq. (1.23) the smallest length resolvable by a microscope is given by $d = \lambda/\sin\phi$ and thus the *uncertainty of localization* of an electron can be written as

$$\Delta x \;=\; d \;=\; \frac{\lambda}{\sin\phi}\,. \tag{1.24}$$

It seems as if we chose the wavelength λ to be small enough and $\sin\phi$ to be big, then Δx could become arbitrarily small. But, as we shall see, the accuracy increases at the expense of the momentum accuracy. Why is that? The photons are detected on the screen but their direction is unknown within an angle ϕ resulting in an uncertainty of the electron's recoil within an interval Δ. So we can identify the momentum uncertainty (in the direction of the screen) of the photon with that of the electron

$$\Delta p_{\mathrm{x}}^{\mathrm{e}} \;=\; \Delta p_{\mathrm{x}}^{\mathrm{Photon}} \;=\; p^{\mathrm{Photon}}\,\sin\phi \;=\; \frac{h}{\lambda}\,\sin\phi\,, \tag{1.25}$$

where we inserted the momentum of the photon $p^{\mathrm{Photon}} \;=\; \hbar k \;=\; h/\lambda$ in the last step. Inserting the position uncertainty of the electron from Eq. (1.24) into Eq. (1.25) we get

$$\boxed{\text{Heisenberg's Uncertainty relation:} \qquad \Delta\, x\, \Delta\, p_{\mathrm{x}} \;=\; h}$$

which he received the Nobel prize for in 1932. We will further see in Sect. 2.6 that the accuracy can be increased by a factor 4π and that the above relation can be generalized to the statement

$$\boxed{\Delta x\, \Delta p_{\mathrm{x}} \;\geq\; \tfrac{\hbar}{2}}$$

This is a fundamental principle that has nothing to do with technical imperfections of the measurement apparatus. We can phrase the uncertainty principle in the following way:

Proposition 1.6.1
Whenever a position measurement is accurate (i.e. precise information about the current position of a particle), the information about the momentum is inaccurate – uncertain – and vice versa.

1.6.2 Energy–Time Uncertainty Principle

We now want to construct another uncertainty relation, the energy–time uncertainty, which describes the relation between the uncertainties Δt for the time a physical process lasts and ΔE for the respective energy. Consider for example a wave packet traveling along the x-axis with velocity v. It takes the time Δt to cover the distance Δx. We can thus write

$$\text{energy:} \quad E \;=\; \frac{p^2}{2m}\,, \qquad \text{velocity:} \quad v \;=\; \frac{\Delta x}{\Delta t}\,. \tag{1.26}$$

Calculating the variation ΔE of the energy E and expressing Δt from the right hand side of Eq. (1.26) by the velocity v and substituting $v \;=\; p/m$ we get

$$\text{variation:} \quad \Delta E \;=\; \frac{p}{m}\Delta p, \qquad \text{time period:} \;\; \Delta t \;=\; \frac{\Delta x}{v} \;=\; \frac{m}{p}\,\Delta x\,. \tag{1.27}$$

The right hand side represents the period of time where the wave is localizable. When we now multiply Δt with ΔE we arrive at:

$$\Delta t\, \Delta E \;=\; \frac{m}{p}\,\Delta x\, \frac{p}{m}\Delta p \;=\; \Delta x\, \Delta p \;\geq\; \frac{\hbar}{2}\,, \tag{1.28}$$

$$\boxed{\Delta E\, \Delta t \;\geq\; \tfrac{\hbar}{2}}$$

We can conclude that there is a fundamental complementarity between energy and time. An important consequence of the energy–time uncertainty is the finite "natural" width of the spectral lines.

1.7 Double–Slit Experiment

1.7.1 Comparison of Classical and Quantum Mechanical Results

We will now take a look at the double–slit experiment, which is well-known from classical optics and whose interference pattern is completely understood when considering light as electromagnetic waves. The experiment can be performed with massive particles as well but then a rather strange phenomenon occurs. It turns out that it is impossible, *absolutely* impossible, to explain it in a classical way or as Richard Feynman [3] phrased it emphasizing the great significance of the double–slit as *the* fundamental phenomenon of quantum mechanics: " ... the phenomenon [of the double–slit experiment] has in it the heart of quantum mechanics. In reality, it contains the *only* mystery."

The associated experiments have been performed with electrons by Möllenstedt and Sönsson in 1959 [4], with neutrons by Rauch [5] and Shull [6] in 1969 and by Zeilinger et al. in the eighties [7]. More recently, in 1999 and subsequent years, Arndt et al. [8] performed a series of experiments using large molecules, so-called fullerenes.

Classical considerations: Let's consider classical particles that pass through an array of two identical slits and are detected on a screen behind the slits. When either the first slit, the second or both slits are open then we expect a probability distribution to find the particle on the screen for the third case (both open) to be just the sum of the distributions for the first and second case (see left side of Fig. 1.13). We can formally write

$$P^{\text{class}}_{1,2} \;=\; P_1 \;+\; P_2 \,, \tag{1.29}$$

where P_{k} $(k = 1,2)$ is the distribution when the k-th slit is open. For classical objects, like e.g. marbles, Eq. (1.29) is valid (for accordingly high numbers of objects).

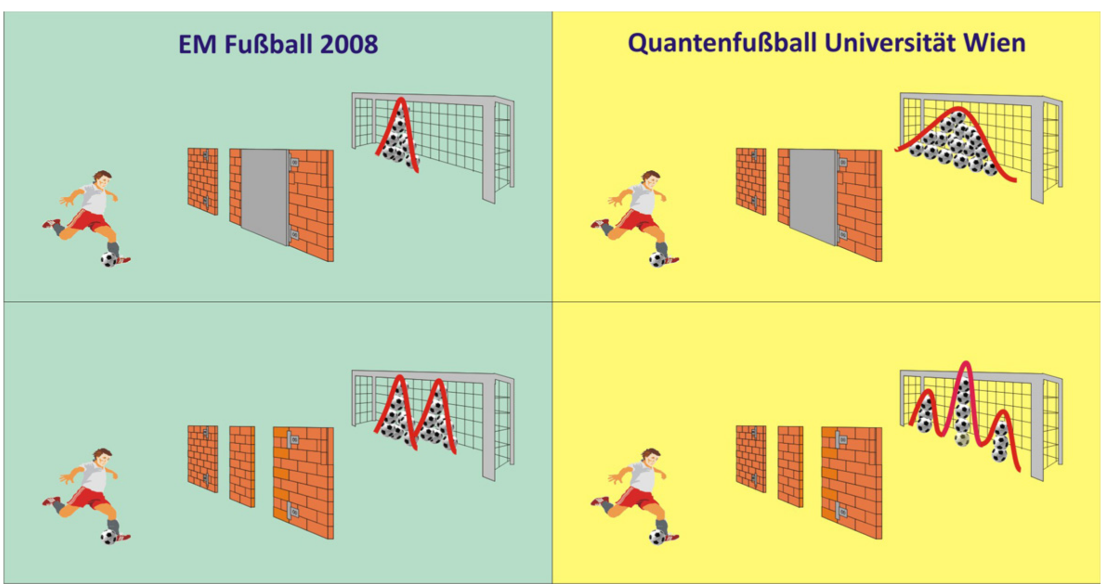

Figure 1.13: Illustration of the double–slit experiment with classical particles (left) and quantum mechanical particles (right); picture used with courtesy of M. Arndt

Quantum version: We now consider the same setup as before, but instead of classical particles we use small objects like electrons or neutrons together with the corresponding detection device and we count the number of clicks from the detector. When either one or the other slit is open, we obtain from the clicking rate some kind of probability distribution similar to the classical case (of course, the intensity need not be a single peak, see for example Fig. 1.12, but the explicit form does not matter here). More important, however, is the case when both slits are open. Then the probability distribution produced is not equal to the sum of the single distributions of either slit as in the classical case, which is illustrated on the right side of Fig. 1.13

$$P^{\,\mathrm{QM}}_{1,2} \neq P_1 + P_2 \,. \tag{1.30}$$

It turns out that the intensity, the probability distribution, resembles an interference pattern of waves. The intensity, the clicking rate, is high where constructive interference of the waves is observed and low where destructive interference occurs.

1.7.2 Interpretation of Quantum Mechanical Results

We now want to formulate the ideas of the previous section in a more rigorous way, concentrating on electrons as representatives of quantum mechanical objects.

We describe the behaviour of the electron by a wave $\psi(x,t)$ which is a complex-valued function.

Proposition 1.7.1 (Born's probability interpretation)
The probability P of finding the electron at a certain position x at the time t, is given by the squared amplitude $|\psi(x,t)|^2 = \psi^*(x,t)\,\psi(x,t)$ – the intensity.

For this interpretation of the wave function Max Born was awarded the 1954 Nobel prize.

From Prop. 1.7.1 we then have the following probability distributions:

$$\begin{aligned} &\text{slit 1 open} \quad & P_1 &= |\psi_1|^2 \\ &\text{slit 2 open} \quad & P_2 &= |\psi_2|^2 \\ &\text{slit 1 and 2 open} \quad & P &= |\psi|^2 = |\psi_1 + \psi_2|^2 = |\psi_1|^2 + |\psi_2|^2 + \underbrace{2\,\mathrm{Re}\,(\psi_1^*\psi_2)}_{\text{interference term}} \end{aligned} \tag{1.31}$$

We see that for both slits open the resulting total wave function is a superposition of the individual wave functions $\psi = \psi_1 + \psi_2$. Thus the total probability corresponding to the intensity is not just the sum of the individual probabilities. From the interference term in Eq. (1.31) – which may have any sign – we conclude that if the term vanishes we won't observe any interference and if it is positive or negative we can expect constructive or destructive interference.

Résumé: An electron as a quantum system passes through the double–slit, then hits a screen or a detector. It produces a very localized lump or causes a click in the detector thus occurring as a definite particle. But the probability for the detection is given by the intensity $|\psi|^2$ of the wave ψ. It is in this sense that an electron behaves like a particle or like a wave.

Remark I: The probability distribution – the interference pattern – is not created, as one could deduce, by the simultaneously incoming electrons but does arise through the interference of the single electron wave function and thus does not change when the electrons pass through the double–slit one by one. The spot of a single electron on the screen occurs totally at random and for few electrons we cannot observe any structure, only when we have gathered plenty of them, say thousands, we can view an interference pattern, which can be nicely seen in Fig. 1.14.

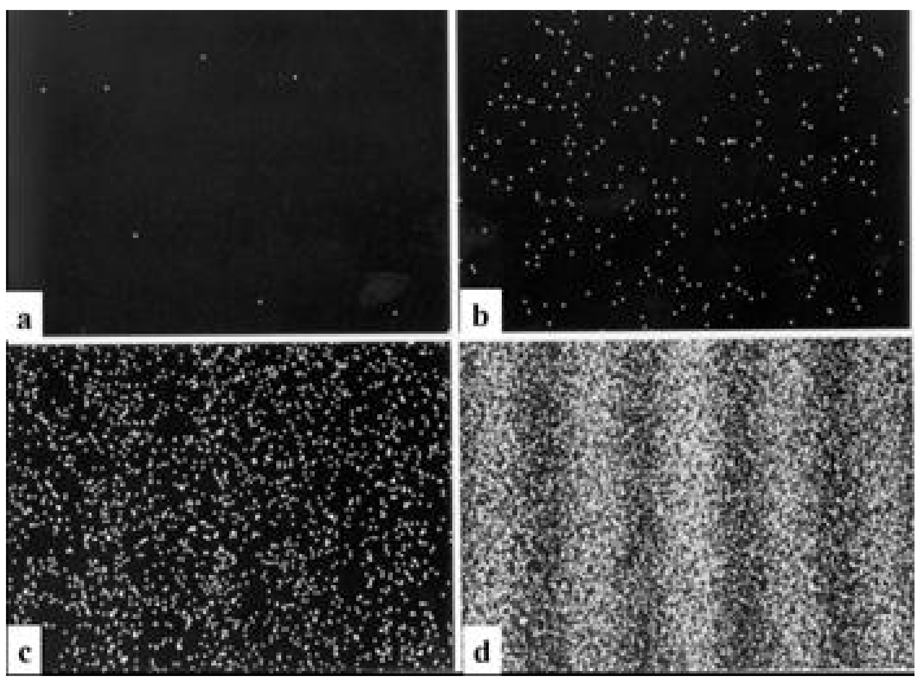

Figure 1.14: Double–slit experiment with single electrons by Tonomura: The interference pattern slowly builds up as more and more electrons are sent through the double slit one by one; electron numbers are a) 8, b) 270, c) 2000, d) 60000; picture from http://de.wikipedia.org/wiki/Bild:Doubleslitexperiment_results_Tanamura_1.gif

Remark II: Path measurement If we wish to gain which-way information, i.e. determine whether the electron passes slit 1 or 2, e.g. by placing a light–source behind the double–slit to illuminate the passing electrons, the interference pattern disappears and we end up with a classical distribution.

Proposition 1.7.2 (Duality)
Gaining path information destroys the wave like behaviour.

It is of crucial importance to recognize that the electron does not split. Whenever an electron is detected at any position behind the double–slit it is always the whole electron and not part of it. When both slits are open, we do not speak about the electron as following a distinct path since we have no such information[7].

1.7.3 Interferometry with C_{60}–Molecules

Small particles like electrons and neutrons are definitely quantum systems and produce interference patterns, i.e. show a wave-like behaviour. We know from Louis de Broglie's hypothesis that every particle with momentum p can be assigned a wavelength. So it's quite natural to ask how big or how heavy can a particle be in order to keep its interference ability, what is the boundary, does there exist an upper bound at all ?

This question has been addressed by the experimental group Arndt, Zeilinger et al. [8] in a series of experiments with fullerenes. Fullerenes are C_{60}–molecules with a high spherical symmetry, resembling a football with a diameter of approximately $D \approx 1\,\mathrm{nm}$ (given by the outer electron shell) and a mass of 720 amu, see Fig. 1.15.

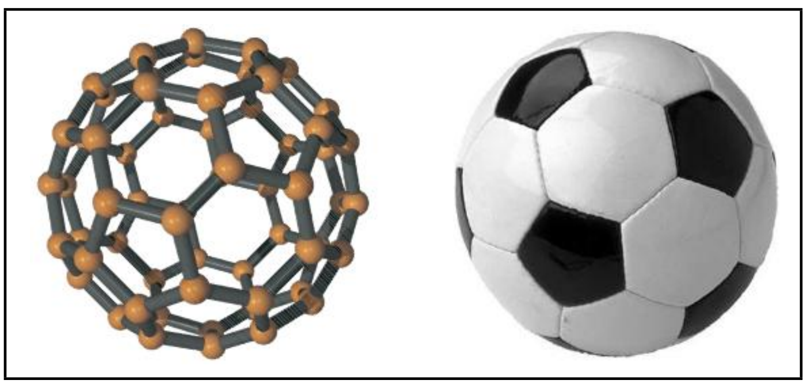

Figure 1.15: Illustration of the structure of fullerenes: 60 carbon atoms are arranged in pentagonal and hexagonal structures forming a sphere analogously to a football; picture used with courtesy of M. Arndt

In the experiment fullerenes are heated to about 900 °K in an oven from where they are emitted in a thermal velocity distribution. With an appropriate mechanism, e.g. a set of

[7] Certain interpretations of quantum mechanics might allow one to assign a definite path to an electron, though one would also need to introduce additional parameters which cannot be sufficiently measured and thus do not improve the predictive power of the theory. For references to the Bohmian interpretation see for example [9] and [10] and for the many worlds interpretation [11]

constantly rotating slotted disks, a narrow range of velocities is selected from the thermal distribution. After collimation the fullerenes pass a SiN lattice with gaps of $a = 50\,\mathrm{nm}$ and a grating period of $d = 100\,\mathrm{nm}$ and are finally identified with help of an ionizing laser detector, see Fig. 1.16.

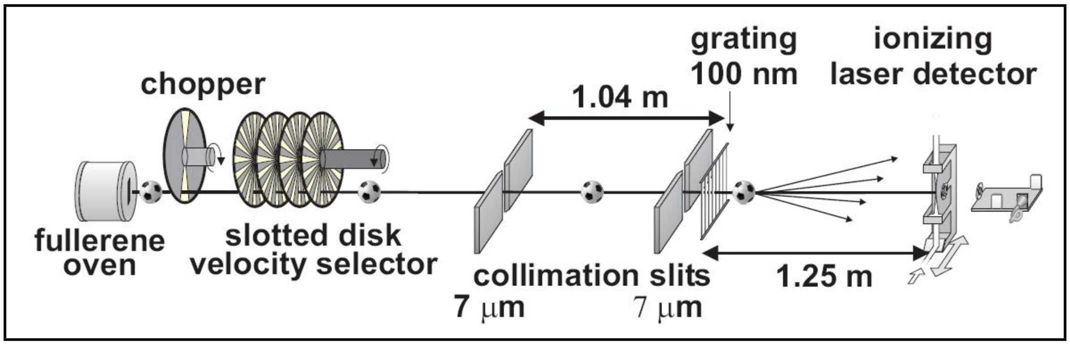

Figure 1.16: Experimental setup for fullerene diffraction; picture by courtesy of M. Arndt

For a velocity $v_{\mathrm{max}} = 220\,\mathrm{m/s}$ the de Broglie wavelength is

$$\lambda_{\mathrm{deBroglie}} = \frac{h}{mv} = 2,5\,\mathrm{pm} \approx \frac{1}{400}\,\mathrm{D}\,, \tag{1.32}$$

thus about 400 times smaller than the size of the particle.

As the angle between the central and the first order intensity maximum is very small (thus $\sin\Theta \approx \Theta$)

$$\Theta = \frac{\lambda_{\mathrm{deBroglie}}}{d} = 25\,\mu\mathrm{rad} = 5\text{”} \tag{1.33}$$

a good collimation is needed to increase the spatial (transverse) coherence. The whole experiment also has to be performed in a high vacuum chamber, pictured in Fig. 1.17, to prevent decoherence of the fullerene waves by collision with residual gas molecules.

The fullerenes are ionized by a laser beam in order to simplify the detection process, where an ion counter scans the target area, see Fig. 1.16.

We can also conclude that the fullerenes do not interfere with each other due to their high temperature, i.e. they are in high modes of vibration and rotation, thus occurring as classically distinguishable objects. Even so to prevent collisions the intensity of the beam is kept very low to ensure a mean distance of the single fullerenes of some mm (which is about 1000 times further than the intermolecular potentials reach). As a side effect of the high temperature the fullerenes emit photons[8] (black body radiation) but, fortunately, these photons don't influence the interference pattern because their wavelengths $\lambda \approx 5 - 20\,\mu\mathrm{m}$ are much bigger than the grating period (the double–slit). Thus we don't get any path information and the interference phenomenon remains.

[8]The probality for photon emission is rather small for the 900 K mentioned, for temperatures higher than 1500 K the probability of emitting (visible) photons is considerably higher but their effects can be neglected for the setup we have described here.

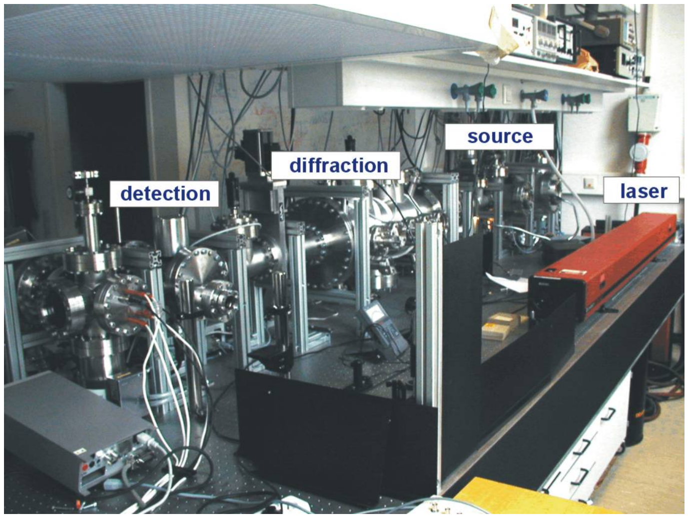

Figure 1.17: Photography of the experimental setup; picture by courtesy of M. Arndt

Looking finally at the result of the fullerene interferometry in Fig. 1.18 we see that the detection counts do very accurately fit the diffraction pattern[9] of the grating, thus demonstrating nicely that quite massive particles behave as true quantum systems.[10]

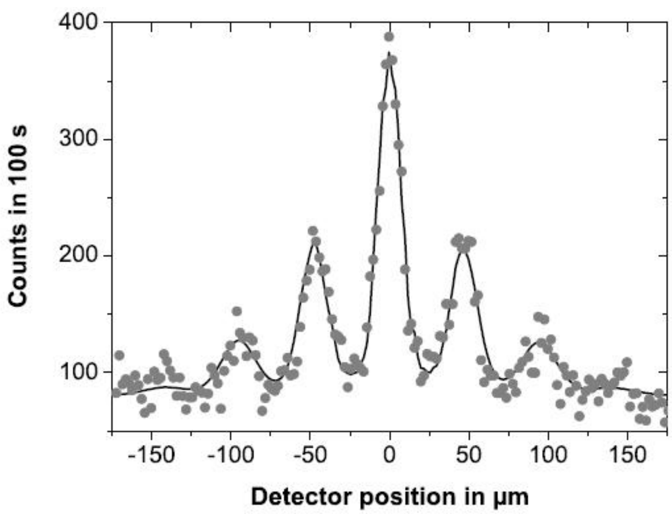

Figure 1.18: Results of the fullerene experiments, see [12]; picture by courtesy of M. Arndt

[9]The inquisitive reader might have noticed that for a grating with a 100 nm period and 50 nm wide slits, the second order diffraction maximum shouldn't exist at all, since the first order minimum of the single slit should cancel the second order maximum of the grating. The reason for its existence lies in the effective reduction of the slit width by Van-der-Waals interaction.

[10]It's quite amusing to notice, while the mass of a fullerene, also called bucky ball, does not agree with the requirements for footballs the symmetry and shape actually does, and furthermore the ratio between the diameter of a buckyball (1 nm) and the width of the diffraction grating slits (50 nm) compares quite well with the ratio between the diameter of a football (22 cm) and the width of the goal (732 cm).