

# Chapter 3

## Quantum Nature of Light and Matter

We understand classical mechanical motion of particles governed by Newton's law. In the last chapter we examined in some detail the wave nature of electromagnetic fields. We understand the occurrence of guided traveling modes and of resonator modes. There are characteristic dispersion relations or resonance frequencies associated with that. In this chapter, we want to summarize some experimental findings at the turn of the 19th century that ultimately lead to the discovery of quantum mechanics, which is that matter has in addition to its particle like properties wave properties and electromagnetic waves have in addition to its wave properties particle like properties. As turns out the final theory, which will be developed in subsequent chapters is much more than just that because the quantum mechanical wave function has a different physical interpretation than a electromagnetic wave only the mathematical concepts used is in many cases very similar. However, this is a tremendous help and guidance in doing and finally understanding quantum mechanics.

### 3.1 Black Body Radiation

In 1900 the physicist Max Planck found the law that governs the emission of electromagnetic radiation from a black body in thermal equilibrium. More specifically Planck's law gives the energy stored in the electromagnetic field in a unit volume and unit frequency range,  $[f, f + df]$  with  $df = 1Hz$ , when the

electromagnetic field is in thermal equilibrium with its surrounding that is at temperature  $T$ . A black body is simply defined as an object that absorbs all light. The best implementation of a black body is the Ulbricht sphere, see Figure 3.1.

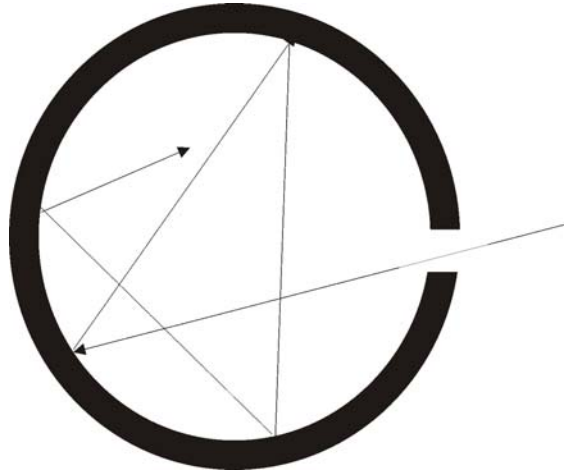


Figure 3.1: The Ulbricht sphere, is a sphere with a small opening, where only a small amount of radiation can escape, so that the interior of the sphere is in thermal equilibrium with the walls, which are kept at a constant temperature. The inside walls are typically made of diffuse material, so that after multiple scattering of the walls any incoming ray is absorbed, i.e. the wall opening is black.

Figure 3.2 shows the energy density  $w(f)$  of electromagnetic radiation in a black body at temperature  $T$ . Around the turn of the 19th century  $w(f)$  was measured with high precision and one was able to distinguish between various approximations that were presented by other researchers earlier, like the Rayleigh-Jeans law and Wien's law, which turned out to be asymptotic approximations to Planck's Law for low and high frequencies.

In order to find the formula describing the graphs shown in Figure 3.2 Planck had to introduce the hypothesis that harmonic oscillators with frequency  $f$  can not exchange arbitrary amounts of energy but rather only in discrete portions, so called quanta. Planck modelled atoms as classical oscillators with frequency  $f$ . Therefore, the energy of an oscillator must be quantized in energy levels corresponding to these energy quanta, which he

found to be equal to  $hf$ , where  $h$  is Planck's constant

$$h = 6.62620 \pm 5 \cdot 10^{-34} J_s. \quad (3.1)$$

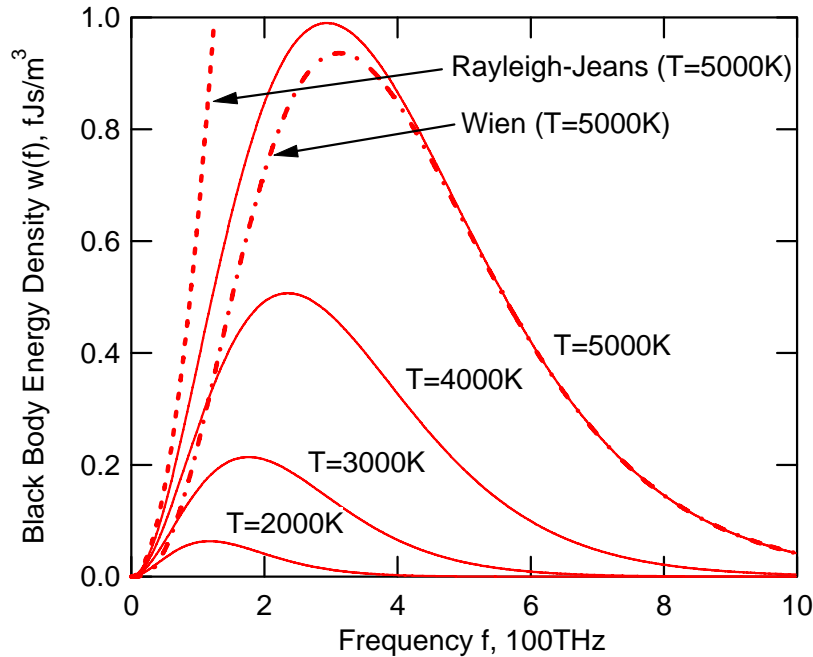


Figure 3.2: Spectral energy density of the black body radiation according to Planck's Law.

As a model for a black body we use now a cavity with perfectly reflecting walls, somewhat different from the Ulbricht sphere. In order to tap of a small but negligible amount of radiation from the inside, a small opening is in the wall. We can make this opening so small that it does essentially not change the internal radiation field. Then the radiation in the cavity is the sum over all possible resonator modes in the cavity. If the cavity is at temperature  $T$  all the modes are thermally excited by emission and absorption of energy quanta from the atoms of the wall.

For the derivation of Planck's law we consider a cavity with perfectly conducting walls, see Figure 3.3.

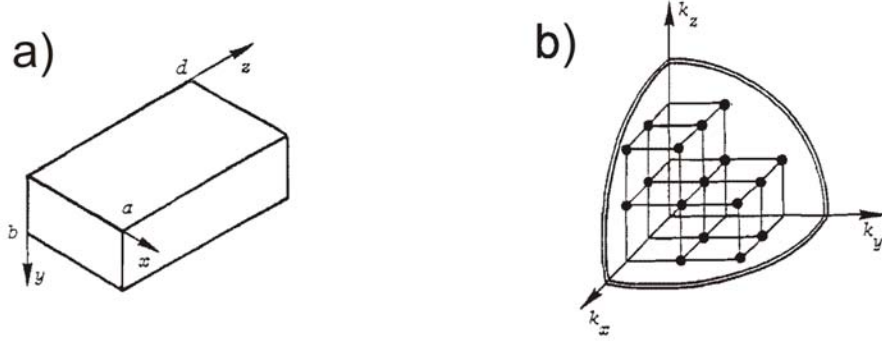


Figure 3.3: (a) Cavity resonator with metallic walls. (b) Resonator modes characterized by a certain  $k$ -vector.

If we extend the analysis of the plan parallel mirror waveguide to find the TE and TM modes of a three-dimensional metallic resonator, the resonator modes are  $TE_{mnp}$ - and  $TH_{mnp}$ -modes characterized by its wave vector components in  $x$ -,  $y$ -, and  $z$ -direction. The resonances are standing waves in three dimensions

$$k_x = \frac{m\pi}{L_x}, \quad k_y = \frac{n\pi}{L_y}, \quad k_z = \frac{p\pi}{L_z}, \quad \text{for } m, n, p = 0, 1, 2, \dots \quad (3.2)$$

An expression for the number of modes in a frequency interval  $[f, f + df]$  can be found by recognizing that this is identical to the number of points in Figure 3.3(b) that are in the first octant of a spherical shell with thickness  $dk$  at  $k = 2\pi f/c$ . The volume occupied by one mode in the space of wave numbers  $k$  is  $\Delta V = \frac{\pi}{L_x} \cdot \frac{\pi}{L_y} \cdot \frac{\pi}{L_z} = \frac{\pi^3}{V}$  with the volume  $V = L_x L_y L_z$ . Then the number of modes  $dN$  in the frequency interval  $[f, f + df]$  in volume  $V$  are

$$dN = 2 \cdot \frac{4\pi k^2 dk}{8 \frac{\pi^3}{V}} = V \frac{k^2 dk}{\pi^2}, \quad (3.3)$$

where the factor of 2 in front accounts for the two polarizations or  $TE$  and  $TH$ -modes of the resonator and the 8 in the denominator accounts for the fact that only one eighth of the sphere, an octant, is occupied by the positive wave vectors. With  $k = 2\pi f/c$  and  $dk = 2\pi df/c$ , we obtain for the number of modes finally

$$dN = V \frac{8\pi}{c^3} f^2 df \quad (3.4)$$

Note, that the same density of states is obtained using periodic boundary conditions in all three dimensions, i.e. then we can represent all fields in terms of a three dimensional Fourier series. The possible wave vectors would range from negative to positive values

$$k_x = \frac{2m\pi}{L_x}, \quad k_y = \frac{2n\pi}{L_y}, \quad k_z = \frac{2p\pi}{L_z} \quad \text{for } m, n, p = 0, \pm 1, \pm 2, \dots \quad (3.5)$$

However, these wavevectors fill the whole sphere and not just one 8-th, which compensates for the 8-times larger volume occupied by one mode. If we imply periodic boundary conditions, we have forward and backward running waves that are independent from each other. If we use the boundary conditions of the resonator, the forward and backward running waves are connected and not independent and form standing waves. One should not be disturbed by this fact as all volume properties, such as the energy density, only depends on the density of states, and not on surface effects, as long as the volume is reasonably large.

### 3.1.1 Rayleigh-Jeans-Law

The excitation amplitude of each mode obeys the equation of motion of a harmonic oscillator. Therefore, classically one expects that each of mode is in thermal equilibrium excute with a thermal energy  $kT$  according to the equipartition theorem, where  $k$  is Boltzmann's constant with

$$k = 1.38062 \pm 6 \cdot 10^{-23} J/K. \quad (3.6)$$

If that is the case the spectral energy density is given by the Rayleigh-Jeans-Law, see Figure 3.2.

$$w(f) = \frac{1}{V} \frac{dN}{df} kT = \frac{8\pi}{c^3} f^2 kT. \quad (3.7)$$

As can be seen from Figure 3.2, this law describes very well the black body radiation for frequencies  $hf \ll kT$  but there is an arbitrary large deviation for high frequencies. This formula can not be correct, because it predicts infinite energy density for the high frequency modes resulting in an "ultraviolet catastrophe", i.e. the electromagnetic field contains an infinite amount of energy at thermal equilibrium.

### 3.1.2 Wien's Law

The high frequency or short wavelength region of the black body radiation was first empirically described by Wien's Law

$$w(f) = \frac{8\pi hf^3}{c^3} e^{-hf/kT}. \quad (3.8)$$

Wien's law is surprisingly close to Planck's law, however it slightly fails to correctly predict the asymptotic behaviour at low frequencies or long wavelengths.

### 3.1.3 Planck's Law

In the winter of 1900, Max Planck found the correct law for the black body radiation by assuming that each oscillator can only exchange energy in discrete portions or quanta. We rederive it by assuming that each mode can only have the discrete energy values

$$E_s = s \cdot hf, \text{ for } s = 0, 1, 2, \dots \quad (3.9)$$

Thus  $s$  is the number of energy quanta stored in the oscillator. If the oscillator is a mode of the electromagnetic field we call  $s$  the number of photons. For the probability  $p_s$ , that the oscillator has the energy  $E_s$  we assume a Boltzmann-distribution

$$p_s = \frac{1}{Z} \exp\left(-\frac{E_s}{kT}\right) = \frac{1}{Z} \exp\left(-\frac{hf}{kT}s\right), \quad (3.10)$$

where  $Z$  is a normalization factor such that the total probability of the oscillator to have any of the allowed energy values is

$$\sum_{s=0}^{\infty} p_s = 1. \quad (3.11)$$

Note, due to the fact that the oscillator energy is proportional to the number of photons, the statistics are exponential statistics. From Eqs.(3.10) and (3.11) we obtain for the normalization factor

$$Z = \sum_{s=0}^{\infty} \exp\left(-\frac{hf}{kT}s\right) = \frac{1}{1 - \exp\left(-\frac{hf}{kT}\right)}, \quad (3.12)$$

which is also called the partition function. The photon statistics are then given by

$$p_s = \exp\left(-\frac{E_s}{kT}\right) \left[1 - \exp\left(-\frac{hf}{kT}\right)\right]^{-1} \quad (3.13)$$

or with  $\beta = \frac{hf}{kT}$

$$p_s = \frac{1}{Z(\beta)} e^{-\beta s}, \quad \text{with } Z(\beta) = \sum_{s=0}^{\infty} e^{-\beta s} = \frac{1}{1 - e^{-\beta}}. \quad (3.14)$$

Given the statistics of the photon number, we can compute moments of the probability distribution, such as the average number of photons in the mode

$$\langle s^1 \rangle = \sum_{s=0}^{\infty} s^1 p_s. \quad (3.15)$$

This first moment of the photon statistics can be computed from the partition function, using the "trick"

$$\langle s^1 \rangle = \frac{1}{Z(\beta)} \frac{\partial^1}{\partial (-\beta)^1} Z(\beta) = Z(\beta) e^{-\beta}, \quad (3.16)$$

which is

$$\langle s \rangle = \frac{1}{\exp \frac{hf}{kT} - 1}. \quad (3.17)$$

With the average photon number  $\langle s \rangle$ , we obtain for the average energy stored in the mode

$$\langle E_s \rangle = \langle s \rangle hf, \quad (3.18)$$

and the energy density in the frequency intervall  $[f, f + df]$  is then given by

$$w(f) = \langle E_s \rangle \frac{dN}{V df}. \quad (3.19)$$

With the density of modes from Eq.(3.4) we find Planck's law for the black body radiation

$$w(f) = \frac{8\pi f^2}{c^3} \frac{hf}{\exp \frac{hf}{kT} - 1}, \quad (3.20)$$

which was used to make the plots shown in Figure 3.2. In the limits of low and high frequencies, i.e.  $hf \ll kT$  and  $hf \gg kT$ , respectively Planck's law asymptotically approaches the Rayleigh-Jeans law and Wien's law.

### 3.1.4 Thermal Photon Statistics

It is interesting to further investigate the intensity fluctuations of the thermal radiation emitted from a black body. If the wall opening in the Ulbricht sphere, see Figure 3.1, is small enough very little radiation escapes through it. If the Ulbricht sphere is kept at constant temperature the radiation inside the Ulbricht sphere stays in thermal equilibrium and the intensity of the radiation emitted from the wall opening in a frequency interval  $[f, f + df]$  is

$$I(f) = c \cdot w(f). \quad (3.21)$$

Thus the intensity fluctuations of the emitted black body radiation is directly related to the photon statistics or quantum statistics of the radiation modes at frequency  $f$ , i.e. related to the stochastic variable  $s$  : the number of photons in a mode with frequency  $f$ . This gives us directly experimental access to the photon statistics of an ensemble of modes or even a single mode when proper spatial and spectral filtering is applied.

Using the expectation value of the photon number 3.17, we can rewrite the photon statistics for a thermally excited mode in terms of its average photon number in the mode as

$$p_s = \frac{\langle s \rangle^s}{(\langle s \rangle + 1)^{s+1}} = \frac{1}{(\langle s \rangle + 1)} \left( \frac{\langle s \rangle}{(\langle s \rangle + 1)} \right)^s, \quad (3.22)$$

The thermal photon statistics display an exponential distribution, see Figure 3.4. Before we move on, lets see how the average photon number in a given mode depends on temperature and the frequency range considered. Figure 3.5 shows the relationship between average number of photons in a mode with frequency  $f$  or wavelength  $\lambda$  and temperature  $T$ .



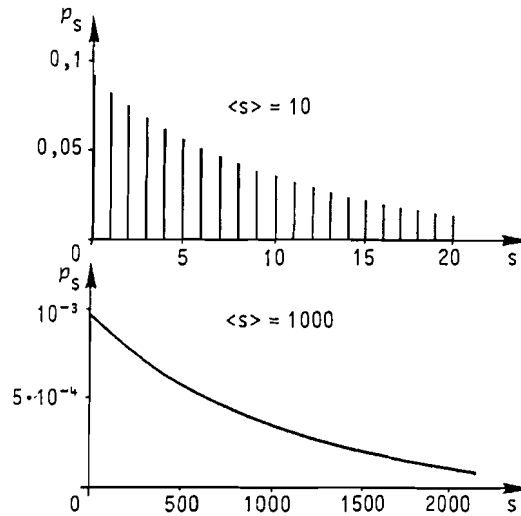


Figure 3.4: Photon statistics of a mode in thermal equilibrium with a mean photon number  $\langle s \rangle = 10$  (a) and  $\langle s \rangle = 1000$  (b).

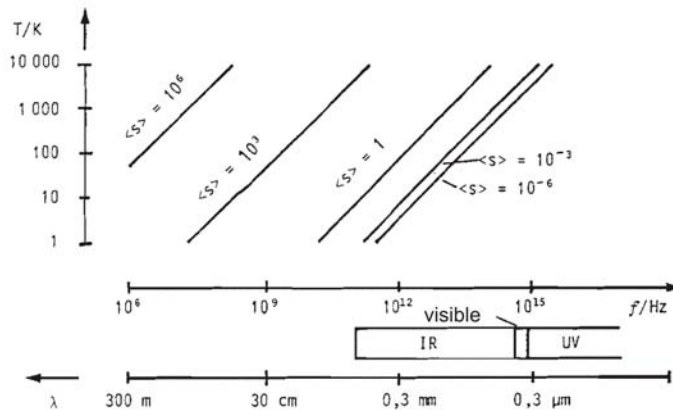


Figure 3.5: Average photon number in a mode at frequency  $f$  or wavelength  $\lambda$  and temperature.

Figure 3.5 shows that at room temperature and microwave frequencies

large numbers of photons are present due to the thermal excitation of the mode. This is the reason that at room temperature the thermal noise overwhelms eventual quantum fluctuations. However, quantum fluctuations are important at high frequencies, which start for room temperature in the far to mid infrared range, where on average much less than one photon is thermally excited.

The variance of the photon number distribution is

$$\sigma_s^2 = \langle s^2 \rangle - \langle s \rangle^2. \quad (3.23)$$

By generalizing Eq.(3.12) to the m-th moment by replacing the exponent 1 by m

$$\langle s^m \rangle = \sum_{s=0}^{\infty} s^m p_s \quad (3.24)$$

$$= \frac{1}{Z} \frac{\partial^m}{\partial (-\beta)^m} Z(\beta), \quad (3.25)$$

we obtain for the second moment

$$\langle s^2 \rangle = 2Z(\beta)^2 e^{-2\beta} - Z(\beta)^2 e^{-2\beta} = 2\langle s^2 \rangle + \langle s \rangle. \quad (3.26)$$

and therefore for the variance of the photon number using Eq.(3.23) is

$$\sigma_s^2 = \langle s \rangle^2 + \langle s \rangle. \quad (3.27)$$

As expected from the wide distribution of photon numbers the variance is larger than the square of the expectation value. This means that if we look at the light intensity of a single mode the intensity is subject to extremely strong fluctuations as large as the mean value. So why don't we see this rapid thermal fluctuations when we look at the black body radiation coming, for example, from the surface of the sun? Well we don't look at a single mode but rather at a whole multitude of modes. Even when we restrict us to a certain narrow frequency range and spatial direction, there is a multitude of transverse modes presence. We obtain for the average total number of photons in a group of modes and its variance

$$\langle s_{tot} \rangle = \sum_{i=1}^N \langle s_i \rangle, \quad (3.28)$$

$$\sigma_{tot}^2 = \sum_{i=1}^N \sigma_i^2. \quad (3.29)$$

Since these modes are independent identical systems, we have

$$\begin{aligned}\langle s_{tot} \rangle &= N \cdot \langle s \rangle. \\ \sigma_{tot}^2 &= N (\langle s \rangle^2 + \langle s \rangle) = \frac{1}{N} \langle s_{tot} \rangle^2 + \langle s_{tot} \rangle.\end{aligned}\quad (3.30)$$

Due to the averaging over many modes, the photon number fluctuations in a large number of modes is reduced compared to its mean value

$$SNR = \frac{\sigma_{tot}^2}{\langle s_{tot} \rangle^2} = \frac{1}{N} + \frac{1}{\langle s_{tot} \rangle}.\quad (3.31)$$

Thus if one averages over many modes and has many photons in these modes the intensity fluctuations become small.

### 3.1.5 Mode Counting

It is interested to estimate the number of modes one is averaging over given a certain emitting surface and a certain measurement time, see Figure 3.6.

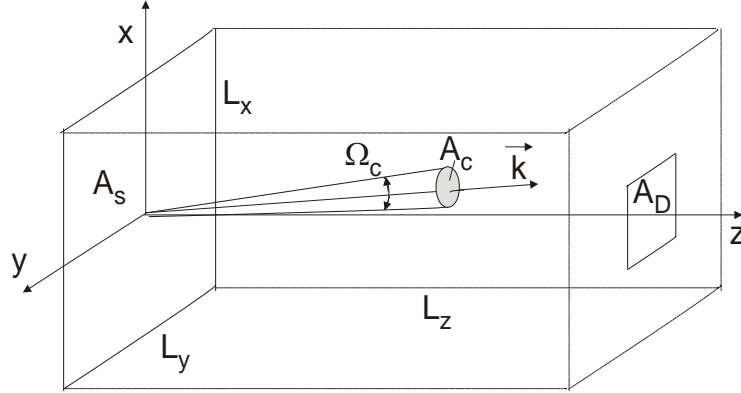


Figure 3.6: Counting of longitudinal and transverse modes excited from a radiating surface of size  $A_s$ .

If the area  $A_s$  is emitting light, it will couple to the modes of the free field. To count the modes we put a large box (universe) over the experimental arrangement under consideration. The emitting surface is one side of the box. The light from this surface, i.e. specifying the transverse electric and magnetic fields, couples to the modes of the universe with wave vectors according to Eq.(3.5).

### Longitudinal Modes

The number of longitudinal modes, that propagate along the positive  $z$ -direction in the frequency interval  $\Delta f$  can be derived from  $\Delta k = (2\pi/L_z) \Delta N$  and  $\Delta k = (2\pi/c_0) \Delta f$

$$\Delta N = \frac{L_z}{c_0} \Delta f, \quad (3.32)$$

or using the propagation or measurement time over which the experiment extends

$$\tau = L_z/c_0, \quad (3.33)$$

we obtain for the number of longitudinal modes that are involved in the measurement that is carried out over a time interval  $\tau$  and a frequency range  $\Delta f$

$$\Delta N = \tau \Delta f . \quad (3.34)$$

### Transverse Modes

The free space modes that arrive at the detector area  $A_D$  will not only have wave vectors with a  $z$ -component, but also transverse components. Lets assume that the detector area is far from the emitting surface, and we consider only the paraxial plane waves. The wave vectors of these waves at a given frequency or free space wave number  $k_0$  can be approximated by

$$\vec{k}_{mn} = \left( \frac{2\pi m}{L_x}, \frac{2\pi n}{L_y}, k_0 \right) \quad \text{with } m, n = 0, 1, 2, \dots \quad (3.35)$$

where  $m$  and  $n$  are transverse mode indices. Then one mode occupies the volume angle

$$\begin{aligned} \Omega_c &= \frac{4\pi^2}{L_x L_y k_0^2}, \\ &= \lambda_0^2 / A_s . \end{aligned} \quad (3.36)$$

If the modes are thermally excited, the radiation in individual modes is uncorrelated. Therefore, if there is a detector at a distance  $r$  then only the field within an area

$$A_c = r^2 \Omega_c , \quad (3.37)$$

is correlated. If the photodetector has an area  $A_d$ , then the number of transverse modes detected is

$$N_t = A_d/A_c. \quad (3.38)$$

The total number of modes detected is

$$N_{tot} = \frac{A_d}{A_c} \tau \Delta f = \frac{A_d A_s}{r^2 \lambda_0^2} \tau \Delta f. \quad (3.39)$$

Note, that there is perfect symmetry between the area of the emitting and receiving surface. The emitter and the receiver could both be black bodies. If one of them is at a higher temperature than the other, there is a net flow of energy from the warmer body to the colder body until equilibrium is reached. This would not be possible without interaction over the same number of modes. Thus the formula which is completely unrelated to thermodynamics is necessary to fulfill one of the main theorems of thermodynamics, that is that energy flows from warmer to colder bodies.

## 3.2 Photo-electric Effect

Another strong indication for the quantum nature of light was the photoelectric effect by Lenard in 1903. He discovered that when ultra violet light is radiated on a photo cathode electrons are emitted, see Figure 3.7.

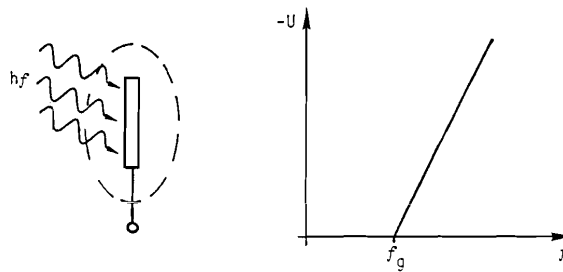


Figure 3.7: Photo-electric effect: (a) Schematic setup and (b) dependence of the necessary grid voltage to suppress the electron current as a function of light frequency.

Lenard surrounded the photo cathode by a grid, which is charged by the emitted electrons up to a voltage  $U$ , which blocks the emission of further electrons. Figure 3.7 shows the blocking voltage as a function of the frequency of the incoming light. Depending on the cathode material there is a cutoff frequency. For lower frequencies no electrons are emitted at all. This frequency as well as the blocking voltage does not depend on the intensity of the light. In 1905, this effect was explained by Einstein introducing the quantum hypothesis for radiation. According to him, each electron emission is caused by a light quantum, now called photon. This photon has an energy  $hf$  and this quantum energy must be larger than the work function  $W_e$  of the material. The remainder of the energy  $m_e v^2/2$  is transferred to the electron in form of kinetic energy. The resulting energy balance is

$$hf = W_e + \frac{1}{2}m_e v^2 \quad (3.40)$$

The kinetic energy of the electron can be used to reach the grid surrounding the photo cathode until the charging energy due to the grid potential is equal to the kinetic energy of the electrons

$$eU = \frac{1}{2}m_e v^2 hf = W_e + \frac{1}{2}m_e v^2 \quad (3.41)$$

or

$$-U = \frac{1}{e}(hf - W_e), \text{ for } hf > W_e. \quad (3.42)$$

This equation explains the empirically found law by Lenard explaining the cutoff frequency and the charge buildup as a function of light frequency. Einstein was first to introduce the idea that the electromagnetic field contains light quanta or photons.

### 3.3 Spontaneous and Induced Emission

The number of photons in a radiation mode may change via emission of photon into the mode or absorption of a photon from the mode by atoms, molecules or a solid state material. Einstein introduced a phenomenological theory of these processes in order to explain how matter may get into thermal equilibrium by interaction with the modes of the radiation field. He considered the interaction of a mode with atoms modeled by two energy levels  $E_1$  and  $E_2$ , see Figure 3.8.

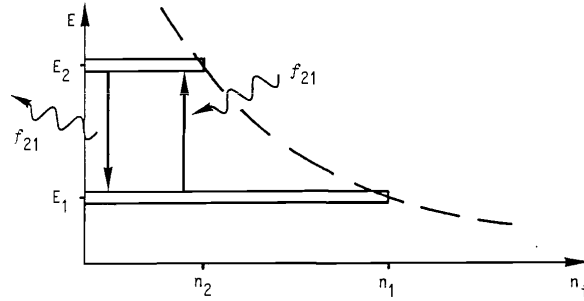


Figure 3.8: Energy levels of a two level atom and populations.

$n_1$  and  $n_2$  are the population densities of these two levels considering a whole ensemble of these atoms. Transitions are possible in the atom between the two energy levels by emission of a photon at a frequency

$$f = \frac{E_2 - E_1}{h} \quad (3.43)$$

Absorption of a photon is only possible if there is energy present in the radiation field. Einstein wrote for the corresponding transition rates, which should be proportional to the population densities and the photon density at the transition frequency

$$-\left. \frac{dn_1}{dt} \right|_{Abs} = \left. \frac{dn_2}{dt} \right|_{Abs} = B_{12} n_1 w(f_{21}). \quad (3.44)$$

The coefficient  $B_{12}$  characterizes the absorption properties of the transition. Einstein had to allow for two different kind of processes for reasons that become clear a little later. Transitions induced by the already present photons or radiation energy as well as spontaneous transitions

$$\left. \frac{dn_1}{dt} \right|_{Em} = -\left. \frac{dn_2}{dt} \right|_{Em} = B_{21} n_2 w(f_{21}) + A_{21} n_2. \quad (3.45)$$

The coefficient  $B_{21}$  describes the induced and  $A_{21}$  the spontaneous emissions. The latter transitions occur even in the absence of any radiation and the corresponding coefficient determines the lifetime of the excited state

$$\tau_{sp} = A_{21}^{-1}, \quad (3.46)$$

in the absence of the radiation field. The total change in the population densities is due to both absorption and emission processes

$$\frac{dn_i}{dt} = \left. \frac{dn_i}{dt} \right|_{Em} + \left. \frac{dn_i}{dt} \right|_{Abs}, \text{ for } i = 1, 2 \quad (3.47)$$

Using Eqs.(3.44) and (3.45) we find

$$-\frac{dn_1}{dt} = \frac{dn_2}{dt} = (B_{12} n_1 - B_{21} n_2) w(f_{21}) - A_{21} n_2. \quad (3.48)$$

In thermal equilibrium the energy density of the radiation field must fulfill the condition

$$w(f_{21}) = \frac{A_{21}/B_{12}}{n_1/n_2 - B_{21}/B_{12}}, \quad (3.49)$$

while the atomic ensemble itself should also be in thermal equilibrium which again should be described by the Boltzmann statistics, i.e. the ratio between the population densities are determined by the Boltzmann factor

$$n_2/n_1 = \exp\left(-\frac{E_2 - E_1}{kT}\right). \quad (3.50)$$

And with it the energy density of the radiation field must be

$$w(f_{21}) = \frac{A_{21}/B_{12}}{\exp\left(\frac{hf_{21}}{kT}\right) - B_{21}/B_{12}}. \quad (3.51)$$

A comparison with Planck's law, Eq.(3.20), gives

$$B_{21} = B_{12}, \quad (3.52)$$

and

$$A_{21} = \frac{8\pi}{c^3} h f_{21}^3 B_{12}. \quad (3.53)$$

Clearly, without the spontaneous emission process it is impossible to arrive at Planck's Law in equilibrium. The spectral energy density of the radiation field can be rewritten with the average photon number in the modes at the transition frequency  $f_{21}$  as

$$w(f_{21}) = \frac{8\pi}{c^3} f_{21}^2 h f_{21} \langle s \rangle, \quad \text{with } \langle s \rangle = \langle s \rangle = \frac{1}{\exp\frac{hf_{21}}{kT} - 1}. \quad (3.54)$$



Or we can write

$$w(f_{21}) = \frac{A_{21}}{B_{12}} \langle s \rangle .$$

With that relationship Eq.(3.45) can be rewritten as

$$\left. \frac{dn_1}{dt} \right|_{Em} = - \left. \frac{dn_2}{dt} \right|_{Em} = A_{21} n_2 (\langle s \rangle + 1) , \quad (3.55)$$

which indicates that the number of spontaneous emissions is equivalent to induced emissions caused by the presence of a single photon per mode. Having identified the coefficients describing the transition rates in the atom interacting with the field from equilibrium considerations, we can rewrite the rate equations also for the non equilibrium situation, because the coefficients are constants depending only on the transition considered

$$\frac{dn_1}{dt} = - \frac{dn_2}{dt} = \frac{1}{\tau_{sp}} [(n_2 - n_1) \langle s \rangle + n_2] . \quad (3.56)$$

With each transition from the excited state of the atom to the ground state an emission of a photon goes along with it. From this, we obtain a change in the average photon number of the modes

$$\frac{d \langle s \rangle}{dt} = V \frac{dn_1}{dt} , \quad (3.57)$$

which is

$$\frac{d \langle s \rangle}{dt} = \frac{V}{\tau_{sp}} [(n_2 - n_1) \langle s \rangle + n_2] . \quad (3.58)$$

Again the first term describes the stimulated or induced processes and the second term the spontaneous processes. As we will see later, the stimulated emission processes are coherent with the already present radiation field that is inducing the transitions. This is not so for the spontaneous emissions, which add noise to the already present field. For  $n_1 > n_2$  the stimulated processes lead to a decrease in the photon number and the medium is absorbing. In the case of inversion,  $n_2 > n_1$ , the photon number increases exponentially. According to Eq.(3.50) inversion corresponds to a negative temperature, which is an indication for a non equilibrium situation that can only be maintained by additional means. It is impossible to achieve inversion by simple irradiation of the atoms with intense radiation. As we see from Eq.(3.58) in steady

state the ratio between excited state and ground state population is

$$\frac{n_2}{n_1} = \frac{\langle s \rangle}{\langle s \rangle + 1}, \quad (3.59)$$

which at most approaches equal population for very large photon number. However, such a process can be exploited in a three or four level system, see Figure 3.9, to achieve inversion.

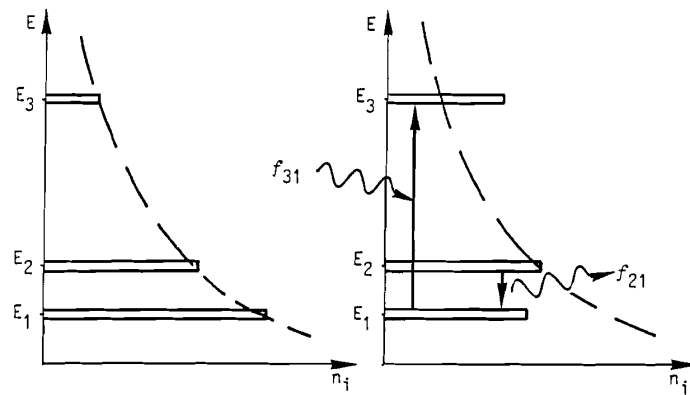


Figure 3.9: Three level system: (a) in thermal equilibrium and (b) under optical pumping at the transition frequency  $f_{31}$ .

By optical pumping population from the ground state can be transferred to the excited level with energy  $E_3$ . If there is a fast relaxation from this level to level  $E_2$ , where level two in contrast has a long lifetime, it is conceivable that an inversion between level  $E_2$  and  $E_1$  can build up. If inversion is achieved radiation at the frequency  $f_{21}$  is amplified.

### 3.4 Matter Waves and Bohr's Model of an Atom

By systematic scattering experiments Ernest Rutherford showed in 1911, that the negative charges in an atom are homogenously distributed in contrast to

the positive charge which is concentrated in a small nucleus about 10,000 times smaller than the atom itself. The nucleus also carries almost all of the atomic mass. Rutherford proposed a model of an atom where the electrons circle the nucleus similar to the planets circling the sun where the gravitational force is replaced by the Coulomb force between the electrons and the nucleus.

This model had many shortcomings. How was it possible that the electrons, which undergo acceleration on their trajectory around the nucleus, do not radiate according to classical electromagnetism, lose energy and finally fall into the nucleus? Due to advances in optical instrumentation the light emitted from thermally excited atomic vapors was known to be in the form of discrete lines. Balmer found in 1885 that these lines could be expressed by the rule

$$\frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \text{ with } n = 3, 4, 5, \dots \quad (3.60)$$

where  $\lambda$  is the wavelength of light and  $R_H = 10.968 \cdot \mu\text{m}^{-1}$  is the Rydberg constant for hydrogen. For  $n = 3$  this corresponds to the red  $H_\alpha$ -line at  $\lambda = 656.3\text{nm}$ , for  $n \rightarrow \infty$  one obtains the wavelength of the limiting line in this series at  $\lambda = 364.6\text{nm}$ , see Figure 3.10.

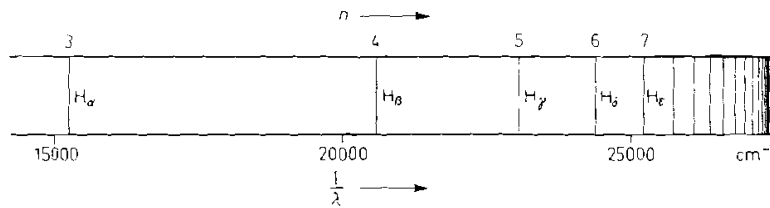


Figure 3.10: Balmer series on a wave number scale.

In the subsequent spectroscopy work further sequences were found:

1. Lyman Series:

$$\frac{1}{\lambda} = R_H \left( \frac{1}{1^2} - \frac{1}{n^2} \right), \text{ with } n = 2, 4, 5, \dots \quad (3.61)$$

2. Balmer Series:

$$\frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \text{ with } n = 3, 4, 5, \dots \quad (3.62)$$

3. Paschen Series:

$$\frac{1}{\lambda} = R_H \left( \frac{1}{3^2} - \frac{1}{n^2} \right), \text{ with } n = 4, 5, 6, \dots \quad (3.63)$$

4. Brackett Series:

$$\frac{1}{\lambda} = R_H \left( \frac{1}{4^2} - \frac{1}{n^2} \right), \text{ with } n = 5, 6, 7, \dots \quad (3.64)$$

5. Pfund Series:

$$\frac{1}{\lambda} = R_H \left( \frac{1}{5^2} - \frac{1}{n^2} \right), \text{ with } n = 6, 7, 8, \dots \quad (3.65)$$

The Lyman series is in the UV-region of the spectrum, whereas the Pfund series is in the far infrared. These sequences can be represented as transitions between energy levels as shown in Figure 3.11.

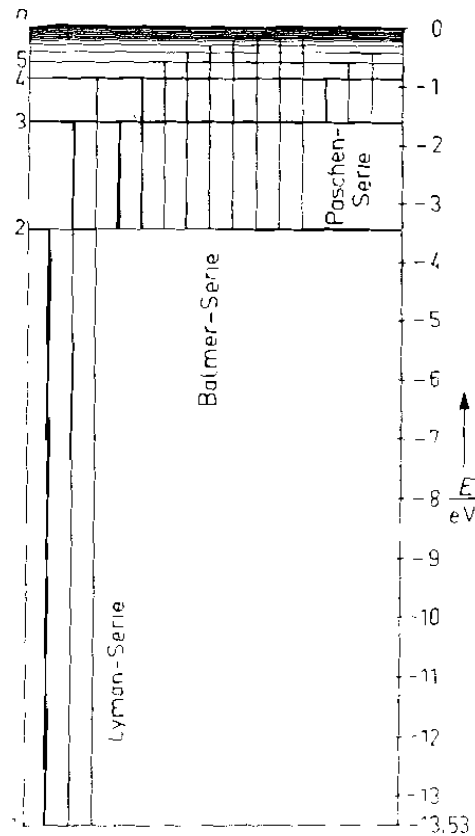


Figure 3.11: Energy level diagram for the hydrogen atom.

In 1913, Niels Bohr found the quantization condition for the electron trajectories in the Hydrogen atom and he was able to derive from that the spectral series discussed above. He postulated that only those electron trajectories are allowed that within one roundtrip around the nucleus have an action equal to a multiple of Planck's quantum of action  $h$ .

$$\oint p \cdot ds = n h, \quad \text{with} \quad n = 1, 2, 3, \dots \quad (3.66)$$

Second, he postulated that the electron can switch from one energy level or trajectory to another one by the emission or absorption of a photon with an

energy equivalent to the energy difference between the two energy levels, see Figure 3.12.

$$hf = \Delta E. \quad (3.67)$$

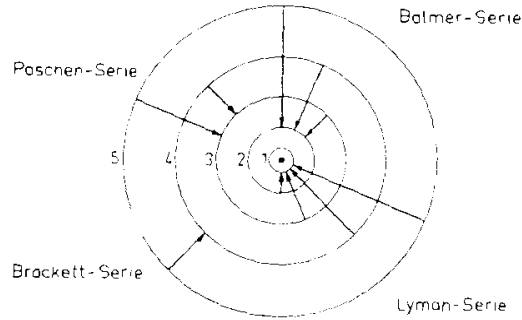


Figure 3.12: Transition between different energy levels in the hydrogen atom.

Assuming a circular trajectory of the electron with radius  $r_n$  around the nucleus, the quantization condition for the electron trajectory (3.66) leads to

$$2\pi r_n m v_n = nh, \quad \text{with } n = 1, 2, 3, \dots \quad (3.68)$$

The other condition for radius and velocity of the electron around the nucleus is given by the equality of Coulomb and centrifugal force at radius  $r_n$ , which leads to

$$\frac{e^2}{4\pi\epsilon_0 r_n^2} = \frac{m v_n^2}{r_n}, \quad (3.69)$$

or

$$v_n^2 = \frac{e^2}{4\pi\epsilon_0 r_n m}. \quad (3.70)$$

Substituting this value for the electron velocity in the squared quantization condition (3.68), we find the radius of the electron trajectories

$$r_n = \frac{\epsilon_0 h^2}{\pi e^2 m} n^2. \quad (3.71)$$

The radius of the first trajectory, called Bohr radius is  $r_1 = 0.529 \cdot 10^{-10} m$ . The velocities on the individual trajectories are

$$v_n = \frac{e^2}{2\epsilon_0 h} \frac{1}{n}. \quad (3.72)$$

The highest velocity is found for the tightest trajectory around the nucleus, i.e. for  $n = 1$ , which can be expressed in terms of the velocity of light as

$$v_1 = \frac{e^2}{2\varepsilon_0 hc} \cdot c = \frac{1}{137} \cdot c, \quad (3.73)$$

where  $\frac{e^2}{2\varepsilon_0 hc} = \frac{1}{137}$  is the fine structure constant.

The energy of the electrons on these trajectories with the quantum number  $n$  is due to both potential and kinetic energy

$$E_{kin} = \frac{1}{2}mv_n^2 = \frac{me^4}{8\varepsilon_0^2 h^2 n^2}, \quad (3.74)$$

$$E_{pot} = -\frac{e^2}{4\pi\varepsilon_0 r_n} = -\frac{me^4}{4\varepsilon_0^2 h^2 n^2}. \quad (3.75)$$

or

$$E_n = E_{kin} + E_{pot} \quad (3.76)$$

$$E_{pot} = -\frac{me^4}{8\varepsilon_0^2 h^2 n^2}. \quad (3.77)$$

Note, the energy of a bound electron is negative. For  $n \rightarrow \infty$ ,  $E_n = 0$ . The electron becomes detached from the atom, i.e. the atom becomes ionized. The lowest and most stable energy state of the electron is for  $n = 1$

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2} = -13.53\text{eV}, \quad (3.78)$$

with correspondes to the ground state in hydrogen. When a transition between two of this energy eigenstates occurs a photon with the corresponding energy is released

$$hf = E_k - E_n, \quad (3.79)$$

$$= -\frac{me^4}{8\varepsilon_0^2 h^2} \left( \frac{1}{k^2} - \frac{1}{n^2} \right). \quad (3.80)$$

### 3.5 Wave Particle Duality

Bohr's postulates were not able to explain all the intricacies of the observed spectra and they couldn't explain satisfactorily the structure of the more complex atoms. This was only achieved with the introduction of wave mechanics. In 1923, de Broglie was the first to argue that matter might also have wave properties. Starting from the equivalence principle of mass and energy by Einstein

$$E_0 = m_0 c_0^2 \quad (3.81)$$

he associated a frequency with this energy accordingly

$$f_0 = m_0 c_0^2/h. \quad (3.82)$$

Since energy and frequency are not relativistically invariant quantities but rather components of a four-vector which has the particle momentum as its other components  $(E_0/c_0, p_x, p_y, p_z)$  or  $(\omega_0/c_0, k_x, k_y, k_z)$ , it was a necessity that with the energy frequency relationship

$$E = hf = \hbar\omega, \quad (3.83)$$

there must also be a wave number associated with the momentum of a particle according to

$$p = \hbar k. \quad (3.84)$$

In 1927, C. J. Davisson and L. H. Germer experimentally confirmed this prediction by finding strong diffraction peaks when an electron beam penetrated a thin metal film. The pictures were close to the observations of Laue in 1912 and Bragg in 1913, who studied the structure of crystalline and polycrystalline materials with x-ray diffraction.

With that finding the duality between waves and particles for both light and matter was established. Duality means that both light and matter have simultaneous wave and particle properties and it depends on the experimental arrangement whether one or the other property manifests itself strongly in the experimental outcome.



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