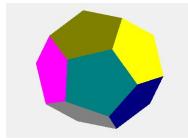


The Hydrogen atom

From Rutherford to Schrödinger

This is an article from my homepage : www.olewitthansen.dk



Contents

1. Rutherford's model of the atom	1
2. The atomic model of Bohr involving the quantum hypothesis	4
3. Classical derivation of the energy of the hydrogen atom.....	7
4. The energy levels in the hydrogen atom according to Bohr.	8
5. The hydrogen spectrum.....	10
6. The quantization of the angular momentum	11
7. The Schrödinger equation	12
8. The angular part of the Schrödinger equation.....	16
8.1 The radial part of the Schrödinger equation.....	17
8.2 The Laguerre polynomials and related Laguerre function.....	18
8.3 Finding the energy levels for the hydrogen atom.	20

1. Rutherford's model of the atom

Although the chemists with success had used the atomic hypothesis of Dalton for half a century, no one had until 1900 acquired a clear picture of the structure of the atoms.

The Englishman J.J. Thomson had discovered the electron and he had determined its mass and its charge. With the knowledge of the positive ions, it was a general assumption that the atoms were composed of positive and negative charge.

Thomson imagined an atom model, (which later has acquired the unjust name "The plum-pudding model"), where the positive charge filled the whole volume of the atom, whereas the electrons sat as raisins in a pudding of positive charge.

However, as it has often been the case in the history of physics, it is not rambling philosophical considerations that make a breakthrough, but rather a well designed experiment.

The groundbreaking experiment was designed and executed by Rutherford in 1910.

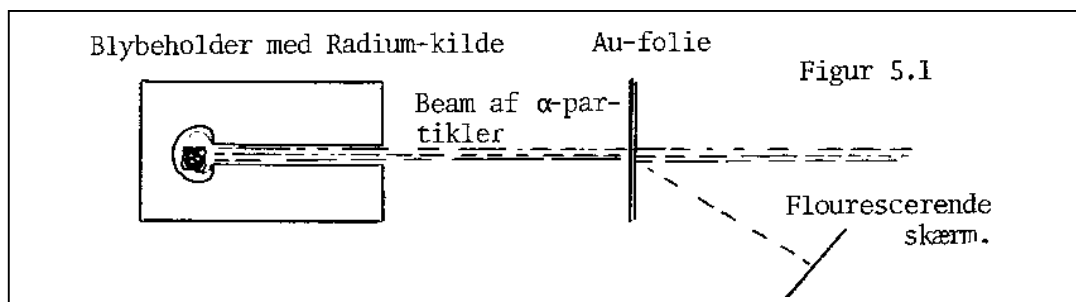
Since it is impossible to view the atoms directly Rutherford designed and executed an experiment, where he bombarded the atoms in a hyper thin gold foil with alpha-particles.

The fast alpha particles were one of the three constituents of radioactive radiation which had been detected and investigated by Becquerel and Curie in the late 1900 century.

The Curies had performed experiments, deflecting alpha particles in electric and magnetic fields, and they had found that the alpha particles carried two positive elementary charges and had a mass about 4 times of the mass of the hydrogen atom. Since the alpha particles are very quickly slowed down in atmospheric air Rutherford's experiments had to be performed in vacuum.

To register how the alpha particles were scattered after passing the *Au*-foil, (and using classical mechanics), Rutherford hoped to get more insight in the structure of the atom.

Below is schematically shown the setup for Rutherford's experiment.



The alpha source is placed in a lead block, having a narrow pipe to secure a collimated stream of alpha particles. (Alpha particles are completely absorbed in less than one *mm Pb*.)

To observe the scattered alpha particles, Rutherford used a fluorescent screen e.g. a *Zns* screen, which gives a tiny flash of light, when hit by a charged particle. These tiny light flashes could only be registered using a microscope, and only after the sensitivity of the retina of the observer had been strengthened by a stay in complete dark for several hours.

In the first of many experiments, Rutherford found that the major part of the alpha-particles passed through the gold foil without deflection.

This observation was in some agreement with a “soft” atomic model, in which the positive charge of the atom is smeared out over its entire volume.

Almost by accident, because he had turned the microscope about 90^0 , he observed that a few alpha particles had a deflection of larger angles, 30 degrees or more.

This observation was, however, in absolute contradiction to the conception of a “soft” atom model, since the “soft” atom model, being bombarded with alpha particles, could be compared to firing rifle bullets into a block of wax or another soft material.

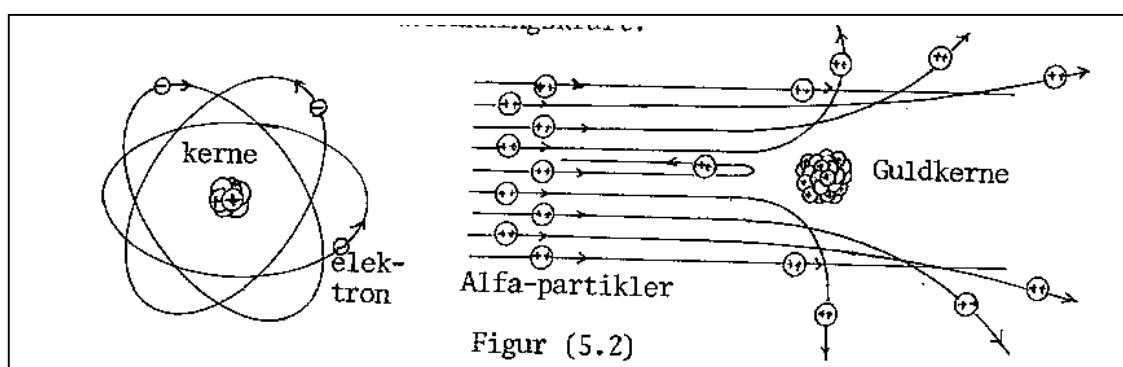
The electric repulsive force which is required to give an alpha particle a large deflection angle, must necessarily be very large, and since the electrical repulsion is inversely proportional to the square of the distance between the alpha particle and the atom, then the positive charge in the atom had to be located in a very small region.

From the results of the experiments Rutherford thus concluded that the positive charge, and thereby its mass of the atom had to be concentrated in an extremely tiny region compared to the size of the atom.

Rutherford therefore made the conjecture which afterwards appears obvious, (once you hear it for the first time) that analogous to the planetary system, where the much smaller planets orbit around the massive sun, the small electrons orbit around the massive nucleus of the atom.

The tremendous difference between the planetary system and the atom is of course the size of the forces involved.

The gravitational constant has the value $G = 6.67 \cdot 10^{-11}$ (SI-units), whereas the corresponding constant in Coulombs law has the value $9 \cdot 10^9$ (SI-units). The ratio between these two constants more or less also reflects the ratio between the size of the planetary system and the size of atoms. Below is schematically shown how one may picture the structure of the atom, together with the scattering of alpha particles from an *Au* nucleus.



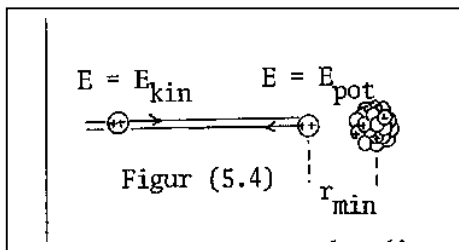
Although remarkably simple (when you think of it), Rutherford’s model of the atom was a radical breakthrough. For the first time it was conceived that the atom had a structure consisting of a positive nucleus with orbiting electrons. Furthermore the stability of the atom could be explained (but not quite) by the already well known Coulombs law.

Since Coulombs law and the law of gravitation are mathematically identical the orbits of the electrons will be elliptically. On the other hand the alpha particles which are not bound to the atomic nucleus will perform hyperbolic trajectories.

Building on his atomic model, based on Coulombs law, Rutherford could make theoretical calculations of the so called *cross sections* (the fraction of the scattered particles that hits an area on a sphere having the target as its centre). His derivation of the deflection angle of the alpha particles will, however, be deferred to the section on nuclear physics.

Since the experimental results came out in perfect agreement with theory it was a tremendous success for Rutherford's model.

Based on the agreement of theory with experiment Rutherford concluded that the alpha particles had not reached the nucleus, since otherwise (unknown) non electrical forces between the alpha particles and the nucleus would play a role.



On these premises Rutherford was able to calculate an upper limit for the size of the nucleus, for example by observing alpha particles from a central impact where the deflection angle is 180° .

To determine the upper limit for the radius of the nucleus, we apply the conservation of energy theorem expressing that the kinetic energy the alpha particle far from the nucleus is equal to its potential energy at its closest position to the nucleus,

where the alpha particle is at rest. The kinetic energy of the alpha particle is: $E_{kin} = \frac{1}{2}mv^2$.

When the alpha particle turns around, it has the distance r_{min} to the nucleus, and it has only potential energy. (We assume that the nucleus is that much heavier than the alpha particle, so that the nucleus is at rest during the impact).

The potential energy of two particles with charges $2e$ (alpha particle) and Ze (Au nucleus) is:

$$(1.1) \quad E_{pot} = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_{min}}$$

Energy conservation then gives:

$$(1.2) \quad \Delta E_{kin} + \Delta E_{pot} = 0 \quad \Leftrightarrow \quad \frac{1}{2}mv^2 = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{r_{min}} \quad \Leftrightarrow \quad r_{min} = \frac{Ze^2}{\pi\epsilon_0 mv^2}$$

If we insert $E_{kin} = 4.78 \text{ MeV}$, which was the energy of the alpha particles used by Rutherford, we may solve (1.2) for r_{min} to give $4.76 \cdot 10^{-14} \text{ m}$.

The unit of length 10^{-15} m is called 1 Fermi (1 fm). The size of the nucleus is between roughly 1 fm to 11 fm . The size of an atom is about 10^{-10} m .

This means that if we enlarge the nucleus to a needle head (1 mm), the outer electrons be found in a distance of 10 meters. (So most of the atom consists of vacuum).

At first sight it appeared that Rutherford's atom model might also account for the emission of light from the atoms.

If an electron orbits the nucleus, then according to the classical theory, there will be emitted electromagnetic radiation. From the Maxwell equations it follows that accelerated charged particles emits electromagnetic radiation.

If a charged particle performs a periodic motion with frequency ν , then the frequency of the radiation is also ν . If a charged particle performs a uniform circular motion with frequency ν , then the emitted light will have the same frequency.

1.3 Example: An estimate of the wavelength for light emitted from a *Na*-atom.

Experimentally the light from the *Na* atom is yellow having a wavelength 689 nm .

We approximate the size of the *Na* atom by the radius in the outmost electron orbit, but the radius can also be estimated from the density of *Na*, and the mass of one mole *Na*.

$M_{Na} = 23 \text{ g/mole}$, and the density is: $\rho = 0.97 \text{ g/cm}^3$. If N_A is Avogadro's number one *Na* atom has the mass:

$m = \frac{M_{Na}}{N_A}$. From the formula: $\rho = \frac{m}{V}$, we may then calculate the volume V of a *Na* atom, and finally we can find

the radius of the atom from the formula for the volume sphere of a sphere: $V = \frac{4}{3}\pi r^3$

$$m = \frac{M}{N_A} \quad \wedge \quad V = \frac{m}{\rho} \quad \wedge \quad V = \frac{4}{3}\pi r^3 \quad \Rightarrow \quad r = \sqrt[3]{\frac{3V}{4\pi}} \quad \Rightarrow \quad r = \sqrt[3]{\frac{3}{4\pi} \frac{M}{\rho N_A}}$$

Inserting the numerical values, we find: $r = 2.1 \cdot 10^{-8} \text{ cm} = 2.1 \cdot 10^{-10} \text{ m}$.

When calculating the frequency in the circular motion, we put the Coulomb force F_e equal to the centripetal force F_c . It will, however not be realistic to put the charge of the nucleus equal to Ze , since the nucleus is shielded from the inner electrons. We then make the assumption that the shielding from the inner electrons is complete, so that the electron is only affected by one elementary positive charge. From this we get:

$$(1.4) \quad F_c = F_e \quad \Rightarrow \quad m_e (2\pi\nu)^2 r = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \quad \Rightarrow \quad \nu^2 = \frac{1}{4\pi\epsilon_0} \frac{1}{4\pi^2 m_e} \frac{e^2}{r^2}$$

Inserting the numerical values, we find: $\nu^2 = 6.92 \cdot 10^{29} \text{ Hz}^2$ which gives the frequency $\nu = 8.32 \cdot 10^{14} \text{ Hz}$.

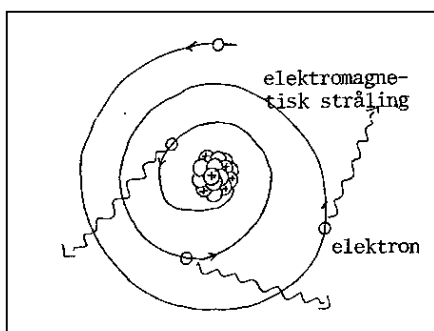
To determine the wavelength we use: $\lambda = \frac{c}{\nu}$, and it results in a wavelength $\lambda = 361 \text{ nm}$.

So we get a wavelength of the right magnitude, but although we have made some crude approximations and simplifications, this theory will never come close to predict the correct value of 632 nm .

Although Rutherford's model explains the structure and stability of the atom, as an atomic planetary system, it is neither able to predict the frequency of the emitted light nor to explain the line spectra of atoms.

2. The atomic model of Bohr involving the quantum hypothesis

Right from the beginning, Rutherford's atomic model was a success, both for its simplicity, and for its foundation on first principles from mechanics and electricity. (The atom is an orbiting system, held together by Coulombs law). It served also as an explanation for well known phenomena as the creation of ions, which had been a part of chemistry for a long time already. A positive ion was merely an atom, which had lost one or two of its outer electrons, and a negative ion was an atom which had attracted and bound one or two extra electrons.



Also the emission of light could be accounted for, since the orbiting electrons (as a consequence of Maxwell's equations), would radiate light with the same frequency as the frequency in the orbit of the electron.

But precisely the explanation of the emission of light from the atoms turned out to be the greatest weakness of the model, since it is a consequence of the Maxwell equations that accelerated charged particles emit electromagnetic radiation.

But that means that the electrons orbiting around the nucleus should *continuously* radiate light.

Furthermore the radiating electrons would lose energy and begin spiralling towards the nucleus, and in less than a millisecond they would sit on the top of the nucleus. Illustrated in figure (6.1) But that we know, has nothing to do with the physical realities. The atoms do not emit light unless they acquire energy from the outside in the form of light or otherwise, and Rutherford's experiment had convincingly demonstrated that the electrons had an orbiting motion far from the nucleus.

Furthermore Rutherford's model failed completely in predicting the characteristic line spectra of the atoms. Even the existence of the line spectra could the model not account for.

It was the Danish physicist Niels Bohr who elaborated on and revised Rutherford's model, so it was brought in accordance with the experience.

Bohr combined Rutherford's atom model with the quantum hypothesis of Planck, since he realized that the line spectra of the atoms corresponded to the energy of the photons. A plausible conjecture, since a photon with a specific energy always has the same frequency: $E_{\text{photon}} = h\nu$.

The discrete values of the frequency of the photons were reproduced in the spectral lines.

Bohr proposed in 1913 his two famous postulates. They were called postulates, because their content could not be derived from any known theory, but merely was an ingenious interpretation of the available experimental data.

1. postulate:

The atom can only exist in a numerable number of so called *stationary states*. In the stationary states the atoms do not emit light. The stationary states may be viewed as selected orbits that the electrons can have. An electron which is bound to the atom is always located in one of these orbits.

2. Postulate:

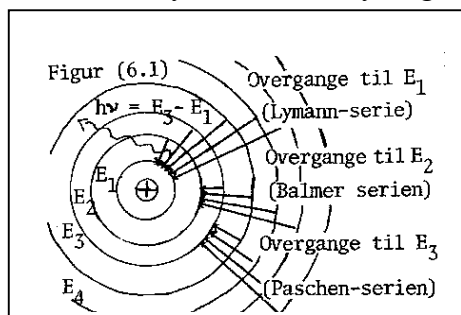
By a transition from one stationary state having energy E_1 to a stationary state having energy E_2 , the atom emits a *photon* given by the *frequency condition*:

$$(2.1) \quad h\nu = E_1 - E_2$$

In the same manner the atom can be excited from the state E_4 to the state E_3 by absorbing a photon with the energy $E = h\nu$. The frequency condition remain the same: This transition may be viewed as if the photon supplies energy to lift an electron from one orbit to another.

$$(2.2) \quad h\nu = E_3 - E_4$$

We shall only look at the Hydrogen atom, being the simplest atom with only one orbiting electron.



In figure (6.1) we have schematically illustrated the transitions to the three lowest energy levels in the hydrogen atom.

The light, which is emitted from transitions to these three levels are named after their inventors.

Transitions to E_1 : The Lyman series, (invisible, because it is in the *UV*- area).

Transitions to E_2 : The Balmer series is visible (and first discovered).

Transitions to E_3 : Paschen series. (invisible, because it is in the infrared region).

In an effort to determine the systematic of the wavelengths of the visible lines in the hydrogen spectrum, Balmer had invented a formula on empirical grounds, shown below.

$$(2.3) \quad \frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right), \quad \text{where } n = 3, 4, 5, \dots$$

It required, however, a stroke of genius that Bohr realized the connection between his two postulates and the empirical Balmer formula. The line of thought is, however, remarkably simple.

From the formula: $\lambda\nu = c$, the energy of a photon can be written as: $h\nu = h\frac{c}{\lambda}$.

If we then multiply the Balmer formula with hc , then the left hand side will represent the energy of a photon. According to the second postulate this should be equal to the difference between the energies in two stationary states. By a minor rewriting in (2.3), we are able to give a conjecture for the expression of the energy levels in the hydrogen atom.

$$(2.4) \quad h\nu = hcR_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right) = -\frac{hcR_H}{n^2} - \left(-\frac{hcR_H}{2^2} \right) (= E_n - E_2)$$

The last parenthesis is the conjecture. From Bohr's postulate the energy of the photon should be written as the difference between two energy levels, and using Balmer's formula it is written as a difference between two quantities, which have the units of energy. It is therefore obvious to make the following identification of the n th energy level:

$$(2.5) \quad E_n = -\frac{hcR_H}{n^2}, \quad \text{where } n = 1, 2, 3, \dots$$

That the energy is negative is what to be expected, since the electron is bound to the nucleus. The energy of the electron also becomes negative in the classical derivation using Coulombs law.

The negative energy is the so called binding energy, that is, the energy required to pull the electron out of the atom. Far away from the atom the relative energy of the electron and the nucleus is zero.

Using Bohr's interpretation, the wavelengths that appear in the Balmer formula correspond to photons emitted in a transition from the n th energy level to the second energy level in the hydrogen atom.

Before 1926 with the appearance of the Schrödinger equation, it was not possible to give a theoretical derivation from first principles that could predict the energy levels in the hydrogen atom.

First we shall make a classical derivation of the energy of the hydrogen atom, next we shall show how Bohr succeeded, (by holding together the classical expression for the energy with the Balmer formula), to express the Rydberg constant R_H by known constants of nature, and thus give a theoretical expression for the energy levels of the hydrogen atom.

3. Classical derivation of the energy of the hydrogen atom

We shall limit ourselves to look at the hydrogen atom, which has a nucleus with one positive elementary charge e , and an orbiting electron with charge $-e$.

We shall assume that the electron performs a uniform circular motion with radius r , and that the nucleus is that heavy compared to the electron that it can be considered as being at rest.

The classical expression for the energy of the electron can then be calculated as follows:

$$(3.1) \quad E = E_{kin} + E_{pot} \quad \text{where} \quad E_{pot} = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \quad \text{and} \quad E_{kin} = \frac{1}{2}mv^2$$

The mass of the electron is m and v is its velocity. E_{kin} can then be expressed by the radius in the circular motion, if we put the centripetal force F_c equal to the Coulomb force F_e .

$$(3.2) \quad F_e = F_c \quad \Leftrightarrow \quad \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} = m \frac{v^2}{r} \quad \Rightarrow \quad \frac{1}{2}mv^2 = \frac{1}{8\pi\epsilon_0} \frac{e^2}{r}$$

$$(3.3) \quad E = E_{pot} + E_{kin} = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} + \frac{1}{8\pi\epsilon_0} \frac{e^2}{r} = -\frac{1}{8\pi\epsilon_0} \frac{e^2}{r}$$

We notice that $|E| = E_{kin}$, but apparently the expression (3.3) has very little resemblance with (2.3), which Bohr deduced from the Balmer formula. We can only observe that both expressions are negative and they both go to zero in the limits: $r \rightarrow \infty$ and $n \rightarrow \infty$.

We also notice that the classical expression for the energy of the atom is a continuous function of r having its maximum zero.

The expression for the energy levels derived by Bohr, however, consists of infinity of discrete values. For large n , however, the levels are very close to each other and in the limit $n \rightarrow \infty$ the energy levels almost lie continuously.

This observation was exploited by Bohr to establish his "*principle of correspondence*".

Since the classical theory is valid on the macroscopic scale and the quantum mechanic description of nature is valid on the atomic scale, there had to be a limit, where both descriptions could account for the physics of particles, that is, there had to be a correspondence (a bridge) between

the classical and the quantum mechanical description. Although this seems logical enough, it was certainly more intriguing to carry the idea out in a theoretical framework.

However, Bohr succeeded administrating great cunning, and using the principle of correspondence to make a calculation of the Rydberg constant, and thereby obtain a purely theoretical expression for the energy levels in the hydrogen atom.

4. The energy levels in the hydrogen atom according to Bohr.

According to Rutherford's model of the atom, the emitted radiation should have the same frequency as the frequency of the electrons in their motion around the nucleus.

If the electron performs a uniform circular motion, we shall express this frequency by the energy.

$$(4.1) \quad \nu = \frac{v}{2\pi r} \quad \wedge \quad E_{kin} = \frac{1}{2}mv^2 \quad \Rightarrow \quad \nu = \frac{1}{2\pi r} \sqrt{\frac{2E_{kin}}{m}} = \frac{1}{2\pi r} \sqrt{2|E|}$$

In the last expression we have applied that $|E| = E_{kin}$ as mentioned in (3.3). Using (3.3) we may also express the electrons radius by the energy, obtaining an expression for the frequency solely by the energy.

$$(4.2) \quad |E| = \frac{1}{8\pi\epsilon_0} \frac{e^2}{r} \quad \Rightarrow \quad r = \frac{1}{8\pi\epsilon_0} \frac{e^2}{|E|}$$

$$r = \frac{1}{8\pi\epsilon_0} \frac{e^2}{|E|} \quad \wedge \quad \nu = \frac{1}{2\pi r} \sqrt{\frac{2|E|}{m}} \quad \Rightarrow \quad \nu = \frac{4\epsilon_0}{e^2} \sqrt{\frac{2|E|^3}{m}}$$

Since the motion of the electrons is not necessarily a uniform circular motion, but just a periodic motion with period ν , it is a consequence of the Maxwell equations that the light can also be emitted with frequencies $2\nu, 3\nu, 4\nu, \dots$ the so called overtones. This is equivalent to the modes of a suspended string performing periodic oscillations.

With this amendment, we obtain from *classical mechanics* the frequencies for light emitted from the hydrogen atom.

$$(4.3) \quad \nu = \frac{4\epsilon_0}{e^2} \sqrt{\frac{2|E|^3}{m}} p, \quad \text{where } p = 1, 2, 3, \dots$$

Bohr believed that the Balmer formula was actually the correct theoretical formula for the wavelength of the light emitted from the hydrogen atom and not just an interpolation formula.

Otherwise a comparison with the classical theory would also have been meaningless.

We have already seen how Bohr managed to find the energy levels of the hydrogen atom from the Balmer formula.

$$(4.4) \quad E_n = -\frac{hcR_H}{n^2}, \quad \text{where } n = 1, 2, 3, \dots$$

At the transition from the n th to the m th stationary state, there is emitted a photon with a frequency given by the frequency condition according to Bohr's 2. postulate.

$$(4.5) \quad h\nu = E_n - E_m = hcR_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right) \quad \Rightarrow \quad \nu = cR_H \left(\frac{1}{m^2} - \frac{1}{n^2} \right)$$

The purpose of Bohr's idea, the correspondence principle, was that there existed a limit (the correspondence (bridge) to the classical physics), where both descriptions could be applied although the formulas looked quite different.

Bohr assumed that the limit should be sought for very large values of m and n , since the energy levels in the Balmer formula lie very close in this limit.

We therefore consider a transition from the $n+p$ 'th to the n th level, where n is a very large number, and $p \ll n$.

$$(4.6) \quad \nu = cR_H \left(\frac{1}{n^2} - \frac{1}{(n+p)^2} \right) = cR_H \left(\frac{(n+p)^2 - n^2}{n^2(n+p)^2} \right) \approx cR_H \frac{2p}{n^3}$$

To obtain the last expression, we have neglected p^2 compared to n^2 in the numerator, and replaced the denominator by n^4 . We then obtain the following expression for the frequencies.

$$(4.7) \quad \nu = cR_H \frac{2cR_H}{n^3} p, \quad p = 1, 2, 3, \dots$$

From (8.4) we may then express n by the energy $|E|$, and we just write E instead of E_n .

$$|E| = \frac{hcR_H}{n^2} \quad \Rightarrow \quad n = \sqrt{\frac{hcR_H}{|E|}}$$

Inserting this result in (8.7), we can express the frequency of the emitted light solely by the energy of the electron, Rydberg's constant and other known constants of nature.

$$(4.8) \quad \nu = \frac{2cR_H}{\left(\sqrt{\frac{hcR_H}{|E|}} \right)^3} p = \frac{2}{h} \sqrt{\frac{|E|^3}{hcR_H}} p \quad \text{where} \quad p = 1, 2, 3, \dots$$

By a comparison between the formula (4.3) (the classical calculation) and (4.8) the quantum physical calculation, we then realize that the two expressions are equal if:

$$(4.9) \quad \frac{4\varepsilon_0}{e^2} \sqrt{\frac{2|E|^3}{m}} p = \frac{2}{h} \sqrt{\frac{|E|^3}{hcR_H}} p$$

This equation obtained by means of the correspondence principle allows us to give an expression for the Rydberg constant by means of already known constants of nature.

$$(4.10) \quad \frac{32\varepsilon_0^2}{e^4 m} = \frac{4}{R_H h^3 c} \quad \Rightarrow \quad R_H = \frac{me^4}{8\varepsilon_0^2 ch^3}$$

The value of R_H calculated from the formula above turned out to be in excellent agreement with the earlier experimental determination.

For the first time someone had succeeded in obtaining a formula for the energy of the stationary states in the hydrogen atom on a purely theoretical basis.

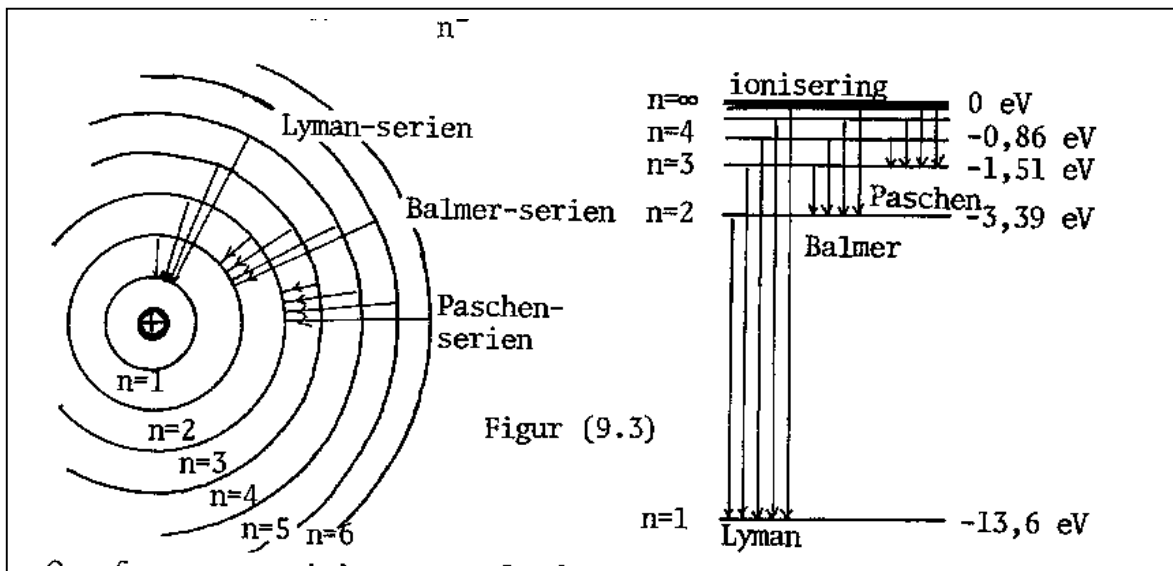
5. The hydrogen spectrum

According to Bohr, the energy levels of the hydrogen atom are given by:

$$(5.1) \quad E_n = -\frac{hcR_H}{n^2} = -\frac{me^4}{8\varepsilon_0^2 h^2 n^2}, \quad n = 1, 2, 3, \dots$$

Evaluating the constant, we find the numerical values for the energy levels.

$$(5.2) \quad E_n = -\frac{13.6 \text{ eV}}{n^2}, \quad n = 1, 2, 3, \dots$$



Above is a schematic illustration of the energy levels in hydrogen. The spectral lines for the transitions to the level E_2 is the Balmer series.

The wavelength for the first line in the Balmer series may be calculated from the formula:

$$h\nu = E_3 - E_2 = -13.6 \text{ eV} \left(\frac{1}{3^2} - \frac{1}{2^2} \right) = 1.89 \text{ eV}$$

$$\lambda = \frac{c}{\nu} = \frac{hc}{1.89 \text{ eV}} = 656 \cdot 10^{-9} \text{ m} = 656 \text{ nm} \quad (\text{The famous red line})$$

In a similar manner one may evaluate the wavelengths of the other spectral lines in the Balmer series.

The spectral lines coming from transitions to the ground state $E_1 = -13.6 \text{ eV}$ are all outside the visible area. For example we can evaluate $E_2 - E_1 = 13.6 \text{ eV} - 3.4 \text{ eV}$, which gives a wavelength of 122 nm deep into the ultraviolet region.

The spectral lines which correspond to transitions to the ground level are called the Lyman series.

The spectral lines, corresponding to the transitions to the energy level $E_3 = -1.51 \text{ eV}$ all belong to the infrared part of the spectrum. Together they are called the Paschen series.

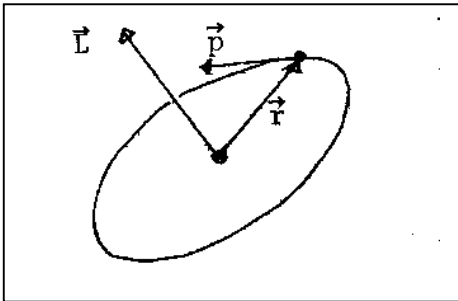
Bohr's theory accounts for the major part of the physics of the hydrogen atom, but the theory was still incomplete, since the theory can neither explain why the transitions take place at all, nor for how long an atom is in an excited state before it decays to the ground state.

Experimentally it is also found that some transitions are far more frequent than others. This is reflected in the variation of the strength of the spectral lines.

6. The quantization of the angular momentum

The application of the correspondence principle to investigate the physics of the atoms is very demanding in respect to ingenuity.

However, Bohr succeeded to obtain the correct result for the energy levels in the hydrogen atom in a more direct way, by assuming the angular momentum of the electron was also quantized.



We remind you that the angular momentum for a particle is defined as:

$$(6.1) \quad \vec{L} = \vec{r} \times \vec{p}$$

Where \vec{r} is the position vector of the particle and \vec{p} is the momentum of the particle.

If especially the particle performs a uniform circular motion, where we have that: $\vec{r} \perp \vec{p}$, we find $L = rp = mrv$.

If we let $L = mrv$ designate the angular momentum of the electron in its motion around the nucleus, Bohr postulated that the angular momentum is quantized, and it can only have the values:

$$(6.2) \quad L = n\hbar = n \frac{h}{2\pi}, \quad \text{where } n = 1, 2, 3, \dots$$

\hbar is a standard designation for Planck's constant divided by 2π .

We shall then proceed to calculate the energy levels in the hydrogen atom using the assumption (6.2). We will apply the expression (3.2) for the kinetic energy of the electron, when it performs a uniform circular motion. From the equations:

$$mvr = n\hbar \quad \text{and} \quad \frac{1}{2}mv^2 = \frac{1}{8\pi\epsilon_0} \frac{e^2}{r}$$

We may solve for r , by eliminating v .

$$v = \frac{n\hbar}{mr} \quad \wedge \quad \frac{1}{2}mv^2 = \frac{1}{8\pi\epsilon_0} \frac{e^2}{r} \quad \Rightarrow \quad \frac{1}{2}m\left(\frac{n\hbar}{mr}\right)^2 = \frac{1}{8\pi\epsilon_0} \frac{e^2}{r} \quad \Rightarrow$$

$$(6.3) \quad r = \frac{4\pi\epsilon_0\hbar^2}{me^2} n^2 \quad n = 1, 2, 3, \dots$$

We see that the quantization of the angular momentum implies that the electron can only be found in some selected orbits, having the radii (6.3). If $n = 1$ is inserted we find a value for the radius, which normally is designated the Bohr radius.

$$(6.4) \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.53 \cdot 10^{-10} \text{ m}$$

If we then insert (6.3) in the classical expression for the energy of the electron, we also find that energy levels are separated.

$$(6.5) \quad E = -\frac{1}{8\pi\epsilon_0} \frac{e^2}{r} \quad \Rightarrow \quad E_n = -\frac{me^4}{8\pi\epsilon_0 \hbar^2} \frac{1}{n^2}, \quad n=1,2,3\dots$$

We notice that (6.5) is identical to (5.1) derived on the basis of the correspondence principle. This confirms that the assumption of the quantization of the angular momentum is correct.

7. The Schrödinger equation

The Schrödinger equation was proposed in 1925 by the Austrian physicist Kurt Erwin Schrödinger and it is the foundation of classical quantum physics in the same manner as Newton's laws are the foundation of classical mechanics. (In this context classical means non relativistic).

It does not at every instant describe a physical system by its position and momentum as in Newtonian mechanics, but rather by a (complex) wave function $\psi = \psi(\vec{x})$, where the density $|\psi|^2 d\vec{x}$ is the probability to find the system in a certain state.

According to the uncertainty principle of Heisenberg, it is not possible to determine the position and momentum simultaneously for a quantum mechanical system. Quantum physics may seem very odd, when you encounter it for the first time – and it certainly is.

The Schrödinger equation describes the dynamical development of a physical system by the wave function.

Compared with Newtonian mechanics the mathematics of the Schrödinger equation is far more complex.

The aim of this section is to solve the Schrödinger equation for what ought to be a simple two body system – the Hydrogen atom. But as you will find it requires rather advanced university mathematics.

The Schrödinger equation in polar coordinates is shown below.

$$(7.1) \quad -\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \left(\frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E \psi$$

First we divide this equation by $-\frac{\hbar^2}{2m}$ and collect the terms on the left side.

$$\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \left(\frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} + \frac{2m}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) \psi = 0$$

The first step in solving the Schrödinger equation is to separate it into three equations corresponding to the three variables (r, θ, φ). This is done in two steps. First we put:

$$(7.2) \quad \psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi)$$

Then we move the factor that does not depend on the other variables outside the differentiation in each term.

$$(7.3) \quad \frac{Y}{r^2} \frac{\partial}{\partial r} r^2 \left(\frac{\partial R}{\partial r} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} + \frac{2m}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) YR = 0$$

Next we multiply the equation by r^2 and divide the equation with YR , rearranging the terms.

$$\frac{1}{R} \frac{\partial}{\partial r} r^2 \left(\frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) + \frac{1}{Y \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{Y \sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} = 0$$

We can now see, that the first two terms do not depend on (θ, φ) , whereas the last two terms do not depend on r . This is only possible if they both are equal to the same constant λ with opposite sign.

$$(7.4) \quad \frac{1}{R} \frac{\partial}{\partial r} r^2 \left(\frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) = \lambda$$

$$\frac{1}{Y \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{Y \sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} = -\lambda$$

Multiplying the equations with R and Y respectively

$$\frac{\partial}{\partial r} r^2 \left(\frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) R - \lambda R = 0$$

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} + \lambda Y = 0$$

The next step is to separate the dependence on the angle θ from the angle φ . Multiplying the second equation by $\sin^2 \theta$, and introducing the functions $\Theta(\theta)$ and $\Phi(\varphi)$ by $Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$.

$$(7.5) \quad \Phi \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \Theta \frac{\partial^2 \Phi}{\partial \varphi^2} + \lambda \sin^2 \theta \Theta \Phi = 0$$

Then by division by $\Theta(\theta)\Phi(\varphi)$, we have:

$$(7.6) \quad \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \lambda \sin^2 \theta + \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \varphi^2} = 0$$

Since the first two terms depend only on θ and the last term only on φ they must be equal to the same constant κ with opposite sign. We then have the two equations:

$$\frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \lambda \sin^2 \theta = -\kappa \quad \text{and} \quad \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \varphi^2} = \kappa$$

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \lambda \sin^2 \theta + \kappa \Theta = 0 \quad \text{and} \quad \frac{\partial^2 \Phi}{\partial \varphi^2} - \kappa \Phi = 0$$

The differential equation

$$\frac{\partial^2 \Phi}{\partial \varphi^2} - \kappa \Phi = 0$$

has the solution:

$$\Phi = c_1 e^{im\varphi} + c_2 e^{-im\varphi}$$

where $m^2 = -\kappa$.

Since φ is the azimuth angle we may choose its zero as we wish, and we therefore put $c_2 = 0$. So the solution becomes:

$$(7.7) \quad \Phi = c_1 e^{im\varphi}$$

The other equation is a bit harder:

$$(7.8) \quad \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \lambda \sin^2 \theta - m^2 \Theta = 0$$

We divide this equation by $\sin^2 \theta$ to get:

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \left(\lambda + \frac{\kappa}{\sin^2 \theta} \right) \Theta = 0$$

We make the substitutions: $x = \cos(\theta)$ and $K(x) = \Theta(\theta)$ and carry out the differentiations, since

$$\frac{\partial \Theta}{\partial \theta} = \frac{\partial \Theta}{\partial x} \frac{\partial x}{\partial \theta} = -\sin(\theta) \frac{\partial \Theta}{\partial x}$$

then we get:

$$-\frac{\partial}{\partial x} \left(\sin \theta (-\sin x) \frac{\partial \Theta}{\partial x} \right) + \left(\lambda - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0 \quad \Leftrightarrow$$

$$\frac{\partial}{\partial x} \left(\sin \theta \sin \theta \frac{\partial \Theta}{\partial x} \right) + \left(\lambda - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0 \quad \Leftrightarrow$$

$$\frac{\partial}{\partial x} \left((1 - \cos^2 \theta) \frac{\partial \Theta}{\partial x} \right) + \left(\lambda - \frac{m^2}{1 - \cos^2 \theta} \right) \Theta = 0 \quad \Leftrightarrow$$

$$\frac{d}{dx} \left((1 - x^2) \frac{dP}{dx} \right) + \left(\lambda - \frac{m^2}{1 - x^2} \right) P = 0 \quad \Leftrightarrow$$

$$(1 - x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left(\lambda - \frac{m^2}{1 - x^2} \right) P = 0$$

To comply with the standard way of writing, we put $\lambda = l(l + 1)$

$$(7.9) \quad (1 - x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left(l(l + 1) - \frac{m^2}{1 - x^2} \right) P = 0$$

This equation is, however, just the associated Legendre equation, which has the solution $P_l^m(x)$.

The Legendre polynomials belong to a rather complex part of university mathematics, and we restrict ourselves to the results that can be found in any textbook on the subject or in the article on my homepage www.olewithansen.dk/Mathematics/Legendre_and_associated_Polynomials.pdf

The Legendre differential equation which appears in several connections in physics is:

$$(1 - x^2) \frac{d^2 y}{dx^2} - 2x \frac{dy}{dx} + n(n + 1)y = 0$$

The solution may be given in several different ways but most compactly by Rodrigues formula:

$$P_n(x) = \frac{1}{2^n n!} \left(\frac{d}{dx} \right)^n (x^2 - 1)^n$$

The first three Legendre polynomials are.

$$P_0(x) = 1,$$

$$P_1(x) = \frac{1}{2} \frac{d}{dx} (x^2 - 1) = x$$

$$P_2(x) = \frac{1}{2^2 2!} \frac{d^2}{dx^2} (x^2 - 1)^2 = \frac{1}{2} x^3 - x$$

$P_0(x)$ is trivially a solution, since it gives: $0 - 2x + 2x = 0$

$P_1(x)$ is a solution, since: $0 - 2x + 1(1 + 1)x = 0$

Then we show that P_2 is a solution to: $(1 - x^2) \frac{d^2 y}{dx^2} - 2x \frac{dy}{dx} + n(n + 1)y = 0$

$$(1-x^2) \frac{1}{2} \frac{d^2}{dx^2} (3x^2-1) - x \frac{d}{dx} (3x^2-1) + 3(3x^2-1) =$$

$$3(1-x^2) - 6x^2 + 9x^2 - 3 = 0$$

To show that the general Legendre polynomial is a solution is more tiresome, however.

We shall now return to the equation for the polar dependence, where $x = \cos(\theta)$, which has the associated Legendre polynomials $P_l^m(x)$ as their solution.

$$(7.10) \quad (1-x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \left(l(l+1) - \frac{m^2}{1-x^2} \right) P = 0$$

The analytic formula for the *associated* Legendre polynomials is:

$$(7.11) \quad P_l^m(x) = (1-x^2)^{\frac{m}{2}} \left(\frac{d}{dx} \right)^m P_l(x)$$

Where $P_l(x)$ is the Legendre polynomial of degree l . The *associated* Legendre polynomials have the following series expansion:

$$(7.12) \quad P_l^m(x) = (1-x^2)^{\frac{m}{2}} \left(a_0 \sum_{n=0}^{\infty} \frac{a_{2n}}{a_0} x^{2n} + a_1 \sum_{n=1}^{\infty} \frac{a_{2n+1}}{a_1} x^{2n+1} \right)$$

Which, by some rather cumbersome calculations leads to the recursion relation.

$$(7.12) \quad a_{n+2} = \frac{(n+m)(m+n+1) - l(l+1)}{(n+1)(n+2)} a_n$$

It is important to notice that when $l = n+m$, then $a_{n+2} = 0$, insuring that all a_{n+4}, a_{n+6}, \dots are zero. In any case for integer l , $P_l^m(x)$ is a polynomial of degree l .

8. The angular part of the Schrödinger equation

We have seen above that the Schrödinger equation can be separated into an angular part and a radial part. The angular part can furthermore be separated into two differential equations corresponding to the polar and azimuth angles. First the azimuth angle.

The equation $\frac{\partial^2 \Phi}{\partial \varphi^2} + \kappa \Phi = 0$ has the solution $\Phi = c e^{im\varphi}$ where $\kappa = -m^2$.

Since the state is supposed to be a stationary we must require:

$$\Phi(\phi + 2\pi) = \Phi(\phi) \Leftrightarrow e^{im(\phi+2\pi)} = e^{im\phi} \Leftrightarrow e^{im2\pi} = 1 \Leftrightarrow m \in Z \quad (m \text{ is an integral number}).$$

The quantum m is the first of the three quantum numbers which characterize the hydrogen (or any atom). It is called the *magnetic* quantum number.

The differential equation for the polar angle is:

$$(8.1) \quad \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \left(l(l+1) - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0$$

The polar equation has the associated Legendre polynomials $P_l^m(x)$ as its solutions.

We have seen that the solutions are always finite polynomials if l is an integer and: $-l \leq m \leq l$

The second quantum number for the hydrogen (or any) atom is l .

The number l it is called the angular momentum quantum number.

The combination of the solutions to the azimuth and the polar equation $\Theta(\theta)\Phi(\varphi)$ are called spherical harmonics. They are denoted:

$$(8.2) \quad Y_{lm}(\theta, \varphi) = P_l^m(\cos \theta) e^{im\varphi} \quad l = 0, 1, \dots \text{ and } -l \leq m \leq l$$

In the operator formulation of the Schrödinger equation, we have:

$$(8.3) \quad H\psi = i\hbar \frac{\partial \psi}{\partial t}$$

where H is the Hamilton operator (the energy).

$$(8.4) \quad H = -\frac{\hbar^2}{2m} (\nabla^2 + V(\vec{x}))$$

The spherical harmonics are simultaneous eigenfunctions to the operators L^2 and L_z , where $\vec{L} = (L_x, L_y, L_z)$ is the angular momentum.

$$(8.5) \quad L^2 = \frac{\hbar^2}{i} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \left(\frac{1}{\sin^2 \theta} \right) \right] \quad \text{and} \quad L_z = \frac{\hbar}{i} \frac{\partial}{\partial \varphi}$$

$$(8.6) \quad L^2 Y_{lm}(\theta, \varphi) = l(l+1)\hbar^2 Y_{lm}(\theta, \varphi) \quad \text{and} \quad L_z Y_{lm}(\theta, \varphi) = m\hbar Y_{lm}(\theta, \varphi)$$

The first few spherical harmonics are:

$$Y_{00} = \sqrt{\frac{1}{4\pi}} \quad Y_{11} = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\varphi} \quad Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta \quad Y_{1,-1} = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\varphi}$$

8.1 The radial part of the Schrödinger equation

$$(8.7) \quad \frac{\partial}{\partial r} r^2 \left(\frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} \left(+ \frac{Ze^2}{4\pi\epsilon_0 r} + E \right) R - \lambda R = 0$$

$$\frac{\partial}{\partial r} r^2 \left(\frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) R - l(l+1)R = 0$$

It seems practical to introduce the substitution: $\chi(r) = rR(r) \Leftrightarrow R(r) = \frac{\chi(r)}{r}$

$$\frac{\partial}{\partial r} r^2 \left(\frac{\partial}{\partial r} \frac{\chi(r)}{r} \right) + \frac{2m^2 r^2}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) \frac{\chi(r)}{r} - l(l+1) \frac{\chi(r)}{r} = 0 \quad \Leftrightarrow$$

$$(8.8) \quad \frac{\partial}{\partial r} (\chi'(r)r - \chi(r)) + \frac{2m^2 r^2}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) \frac{\chi(r)}{r} - l(l+1) \frac{\chi(r)}{r} = 0 \quad \Leftrightarrow$$

$$\chi''(r)r + \chi'(r) - \chi'(r) + \frac{2mr^2}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) \frac{\chi(r)}{r} - l(l+1) \frac{\chi(r)}{r} = 0 \quad \Leftrightarrow$$

$$\chi''(r) + \frac{2m}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) \chi(r) - \frac{l(l+1)}{r^2} \chi(r) = 0$$

Even if you find that the solution of the polar equation involve rather complex mathematics then the solution of the radial equation turns out to be rather heavy university mathematics.

8.2 The Laguerre polynomials and related Laguerre function

The Laguerre differential equation is:

$$(8.9) \quad x \frac{d^2 L_n}{dx^2} + (1-x) \frac{dL_n}{dx} + nL_n = 0$$

The first five Laguerre polynomials, which are solutions to Laguerre's equation are listed below

$$\begin{aligned} L_0(x) &= 1 & L_1(x) &= 1-x & L_2(x) &= x^2 - 4x + 2 \\ L_3(x) &= -x^3 + 9x^2 - 18x + 6 & L_4(x) &= x^4 - 16x^3 + 72x^2 - 96x + 24 \end{aligned}$$

Laguerre polynomials of any order can be calculated, using the generating function:

$$(8.10) \quad L_n(x) = e^x \frac{d^n}{dx^n} (e^{-x} x^n)$$

As an example, we shall generate $L_2(x)$:

$$\frac{d^2}{dx^2} e^{-x} x^2 = \frac{d}{dx} (-e^{-x} x^2 + e^{-x} 2x) = e^{-x} x^2 - e^{-x} 2x - e^{-x} 2x + e^{-x} 2$$

$$e^x \frac{d^2}{dx^2} e^{-x} x^2 = x^2 - 4x + 2$$

The Laguerre polynomials do not form an orthogonal set, but the related *Laguerre functions* do,

$$\phi_n(x) = e^{-x/2} L_n(x)$$

since they are orthonormal on the interval $0 \leq x < \infty$. The Laguerre functions are not solutions to the Laguerre equation, but they are solutions to an equation which is related.

As it was the case with the Legendre equation the Laguerre equation has a derived associated equation, which contain a second index k . The associated Laguerre equation is, (where L_n^k denotes the solutions).

$$(8.11) \quad x \frac{d^2 L_n^k}{dx^2} + (1-x+k) \frac{dL_n^k}{dx} + nL_n^k = 0$$

It reduces to the Laguerre equation when $k=0$. The first few *associated Laguerre polynomials* are listed below: In general $L_n^0(x) = L_n(x)$.

$$L_0^1(x) = 1, \quad L_1^1(x) = -2x + 4, \quad L_2^1(x) = 3x^2 - 18x + 18$$

$$L_0^2(x) = 2, \quad L_1^2(x) = -6x + 18, \quad L_2^2(x) = 12x^2 - 96x + 144$$

Associated Laguerre polynomial are not orthogonal, but associated Laguerre functions of the type:

$$(8.12) \quad \phi_n^k(x) = e^{-x/2} x^{k/2} L_n^k(x)$$

Are orthogonal on the interval $0 \leq x < \infty$, so they make an orthogonal set. The functions $\phi_n^k(x)$, are not solutions to the associated Laguerre equation, but they are solutions to a *related* equation.

In dealing with the radial part of the Schrödinger equation, we are interested in a slightly different associated Laguerre function, where the only difference is that k is replaced with $k+1$, that is the function:

$$(8.13) \quad y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x)$$

These are not only solution to the associated Laguerre equation, but they are also solutions to

$$(8.14) \quad \frac{d^2 y_j^k}{dx^2} + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} x - \frac{k^2-1}{4x^2} k\right) y_j^k = 0$$

The main reason for studying this equation, is that the radial equation may be brought in the form, (8.8), where that the radial function $R(r)$ that we seek is: $R_n^l(r) = \chi_n^l(x)/r$, apart from a normalization constant.

We are now ready to form the connection between the equation above and the radial equation.

For simplicity we put $v = L_j^k(x)$, since the indices do not change in the calculations.

We then show that $y_j^k(x) = y = e^{-x/2}x^{(k+1)/2}v$ satisfy (8,14). We find the first derivative:

$$y' = -\frac{1}{2}e^{-x/2}x^{(k+1)/2}v + e^{-x/2}\left(\frac{k+1}{2}\right)x^{(k+1)/2}v + \frac{1}{2}e^{-x/2}x^{(k+1)/2}v'$$

$$= \left(-\frac{1}{2}v + \left(\frac{k+1}{2x}\right)v + v'\right)e^{-x/2}x^{(k+1)/2}$$

$$y'' = -\frac{1}{2}e^{-x/2}x^{(k+1)/2}\left(-\frac{1}{2}v + \left(\frac{k+1}{2x}\right)v + v'\right) + e^{-x/2}\left(\frac{k+1}{2}\right)x^{(k+1)/2}\left(-\frac{1}{2}v + \left(\frac{k+1}{2x}\right)v + v'\right) +$$

$$e^{-x/2}x^{(k+1)/2}\left(-\frac{1}{2}v' - \left(\frac{k+1}{2x^2}\right)v + \left(\frac{k+1}{2x}\right)v' + v''\right)$$

$$y'' = e^{-x/2}x^{(k+1)/2}\left[-\frac{1}{2}\left(-\frac{1}{2}v + \left(\frac{k+1}{2x}\right)v + v'\right) + \left(\frac{k+1}{2x}\right)\left(-\frac{1}{2}v + \left(\frac{k+1}{2x}\right)v + v'\right) + \left(-\frac{1}{2}v' - \left(\frac{k+1}{2x^2}\right)v + \left(\frac{k+1}{2x}\right)v' + v''\right)\right]$$

Inserting the second derivative and the function $y_j^k(x) = y = e^{-x/2}x^{(k+1)/2}v$ into the equation

$$\frac{d^2 y_j^k}{dx^2} + \left(-\frac{1}{4} + \frac{2j+k+1}{2x}x - \frac{k^2-1}{4x^2}k\right)y_j^k = 0$$

and reducing with the common factor $e^{-x/2}x^{(k+1)/2}$, it still requires some non trivial algebra to arrive at the (correct) result:

$$(8.15) \quad v'' - v' + \frac{k+1}{x} + \frac{j}{x}v = 0 \quad \Leftrightarrow$$

$$xv'' + (k+1-x)v' + jv = 0$$

Which is the associated Laguerre equation:

$$(8.16) \quad \frac{d^2 L_j^k}{dx^2} + (1-x+k)\frac{dL_j^k}{dx} + jL_j^k = 0$$

Since $y = e^{-x/2}x^{(k+1)/2}v = e^{-x/2}x^{(k+1)/2}L_j^k$ then y must be a solution to (8.14):

$$(8.17) \quad \frac{d^2 y_j^k}{dx^2} + \left(-\frac{1}{4} + \frac{2j+k+1}{2x}x - \frac{k^2-1}{4x^2}k\right)y_j^k = 0$$

8.3 Finding the energy levels for the hydrogen atom.

We have reduced the radical equation to:

$$\chi''(r) + \frac{2m}{\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0 r} + E \right) \chi(r) - \frac{l(l+1)}{r^2} \chi(r) = 0 \quad \text{where } R(r) = \chi(r)/r$$

$$(8.18) \quad \frac{d^2 \chi}{dr^2} + \left(\frac{2mZe^2}{4\hbar^2 \pi \epsilon_0 r} + \frac{2m}{\hbar^2} E - \frac{l(l+1)}{r^2} \right) \chi(r) = 0$$

To comply with the associated Laguerre equation, we make the following substitution:

$$\left(\frac{\beta}{2} \right)^2 = -\frac{2mE}{\hbar^2} \quad (\text{Since } E \text{ is negative})$$

The last equation becomes:

$$(8.18) \quad \frac{d^2 \chi}{dr^2} + \left(\frac{2mZe^2}{4\hbar^2 \pi \epsilon_0 r} - \frac{\beta^2}{4} - \frac{l(l+1)}{r^2} \right) \chi(r) = 0$$

Then we make a minor change of variables, since we put $x = r\beta \Leftrightarrow r = \frac{x}{\beta} \Rightarrow dr = \frac{dx}{\beta}$

Using this substitution the equation reads:

$$(8.19) \quad \beta^2 \frac{d^2 \chi}{dx^2} + \left(\frac{2mZe^2}{4\hbar^2 \pi \epsilon_0 x} \beta - \frac{\beta^2}{4} - \frac{l(l+1)}{x^2} \beta^2 \right) \chi(r) = 0 \Rightarrow$$

$$\frac{d^2 \chi}{dx^2} + \left(\frac{2mZe^2}{4\hbar^2 \pi \epsilon_0 x \beta} - \frac{1}{4} - \frac{l(l+1)}{x^2} \right) \chi(r) = 0$$

Then equation (8.19) is equal to (8.17) if

$$l(l+1) = \frac{k^2 - 1}{4} \quad \text{and} \quad \frac{2mZe^2}{4\hbar^2 \pi \epsilon_0 \beta} = \frac{2j + k + 1}{2}$$

$$l(l+1) = \frac{k^2 - 1}{4} \Rightarrow 4l^2 + 4l + 1 = k^2 \Leftrightarrow k^2 = (2l+1)^2 \Rightarrow k = 2l+1$$

Equation (8,19) gives us the conditions of quantisation of the energy, but it requires some development.

$$\frac{2j + k + 1}{2} = \frac{2j + 2l + 1 + 1}{2} = j + l + 1$$

From the discussion on the associated Laguerre polynomials the indices j and l are non negative integers. $J + l + 1$ can therefore assume any integer value from 1. This integer is traditionally denoted n .

$$n = j + l + 1$$

We return to the equation (8.19)

$$\frac{2mZe^2}{4\hbar^2\pi\epsilon_0\beta} = n \Rightarrow \left(\frac{2mZe^2}{4\hbar^2\pi\epsilon_0 n} \right)^2 = \beta^2$$

Since $\left(\frac{\beta}{2}\right)^2 = -\frac{2mE}{\hbar^2}$, we find: $\left(\frac{2mZe^2}{4\hbar^2\pi\epsilon_0 n} \right)^2 = -\frac{8mE}{\hbar^2} \Rightarrow$

$$(8.20) \quad \frac{4m^2Z^2e^4}{16\hbar^4\pi^2\epsilon_0^2n^2} = -\frac{8mE}{\hbar^2} \Rightarrow$$

$$E = -\frac{mZ^2e^4}{32\hbar^2\pi^2\epsilon_0^2n^2} = -\frac{mZ^2e^4}{2\hbar^2(4\pi\epsilon_0)^2n^2} = \frac{Z^2me^4}{8\hbar^2\epsilon_0^2} \frac{1}{n^2}$$

And for the hydrogen atom, where $Z = 1$

$$(8.21) \quad E = -\frac{me^4}{8\hbar^2\epsilon_0^2} \frac{1}{n^2}$$

There is a tradition to express the energy by the Rydberg constant.

$$(8.22) \quad R_H = \frac{me^4}{8ch^3\epsilon_0^2}$$

Then the energy levels become:

$$(8.23) \quad E = -\frac{hcR_H}{n^2}$$

The constant hcR_H has the value 13.6 eV, so the energy levels of the Hydrogen atom are given by:

$$(8.24) \quad E = -\frac{13.6 \text{ eV}}{n^2}$$

The quantity \hbar^2 / me^2 has the dimension of a length. It is called the Bohr radius a_0 .

$$(8.24) \quad a_0 = \frac{\hbar^2}{me^2} = 0.529 \cdot 10^{-8} \text{ m} = 0.529 \text{ \AA}$$