Introduction to Atomic Physics

A concept based on the Schrödinger equation

Textbook for students

by

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1. Standing waves

1.1 Description of standing waves

Every system that can be stimulated to oscillate (a tambourine, a tuning fork or a guitar string) has certain frequencies (called **Eigen-frequencies**) under which it oscillates. E.g. a guitar string oscillates at a certain frequency (its Eigen-frequency) when it is plucked. Because the envelope of the moving string (the maximum of the amplitude) does not change in time, this is called a **standing wave**.

An example for an one dimensional standing wave, very similar to a guitar string, is a string of a certain length which can be stimulated to oscillate with a generator as shown in the picture. In this example the string is 0.53 m long, on the right side is a generator which can move up and down with an adjustable frequency. When the frequency is below 15 Hz one can observe an unstable motion of the string (envelope of the amplitude is time dependent).
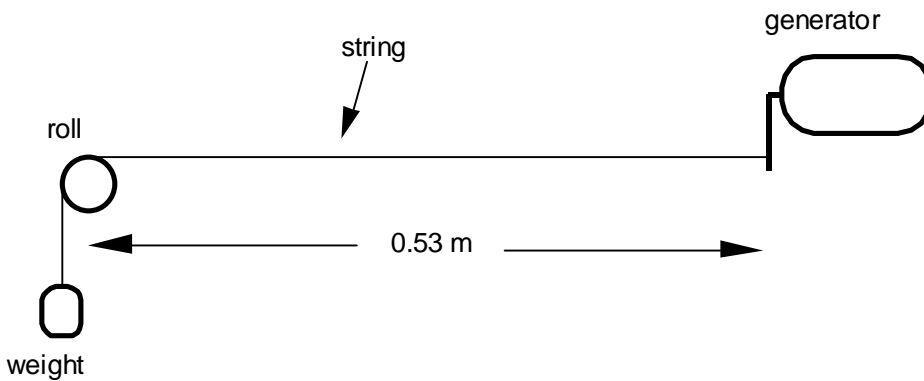

When the frequency is around 15 Hz the picture changes drastically. The envelope of the amplitude of the string becomes time independent and looks like in the picture below for (state n=1). This is called a standing wave. This particular one is called the **ground state** of the string since there are no standing waves below this frequency. There are only two **nodes** at the beginning and the end of the string. The envelope of the amplitude (we want to call it the **amplitude function**) shows only the maximum amplitude of the string.

When the frequency is further increased the string again becomes an unstable motion until the frequency is around 30 Hz. Here one can observe the **second state** (also called **first excited state**) shown in the picture of the state n=2. Again the envelope of the amplitude becomes time independent but has one node between the beginning and the end of the string. This node is in the middle for a uniform string like the one in this example.
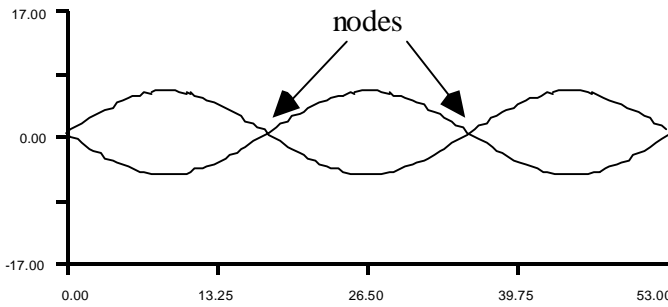
The quantity n is called the **state number** and is a kind of index; each state has its state number; the higher the state number the higher the frequency. The third picture shows the state n=3.
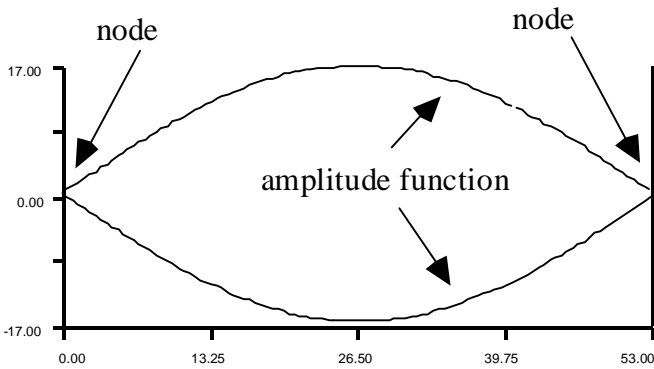
Ground state n=1, f_1=15 Hz
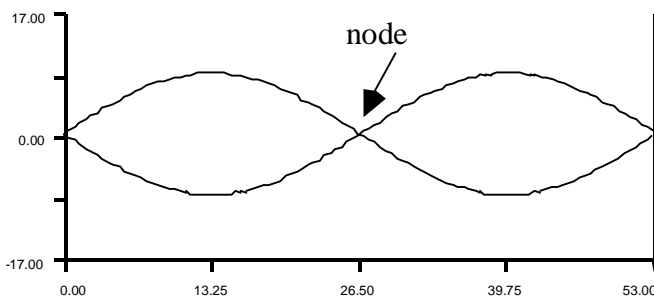
First excited state n=2, f_2=30 Hz

Second excited state n=3, f_3=45 Hz

Summary of the results:
- all systems that can oscillate have **discrete** frequencies f_n (called **Eigen-frequencies**) where they show **standing waves**
- when a standing wave has been found one says that the system is in a **state**
- all states are numerated by **state numbers** n
- a state is characterized by the number of **nodes**
- more general all states are characterized by the shape of the **amplitude function**

In this description the term **state** is a definition in Physics. One says <u>that the system is in a state when it shows a standing wave</u>. A complete description of a standing wave system can be shown graphically in a **level scheme** (the picture below shows not the complete level scheme but only the first three states since there are infinitely many states). Since the envelope of the amplitude is symmetrical to the x-axes one can draw only one function instead of two as shown in the level scheme.

Level Scheme

state number n	Eigen-frequency f_n	amplitude funktion $y_n(x)$

n=3 f_3=45 Hz   second excited state

n=2 f_2=30 Hz   first excited state

n=1 f_1=15 Hz   ground state

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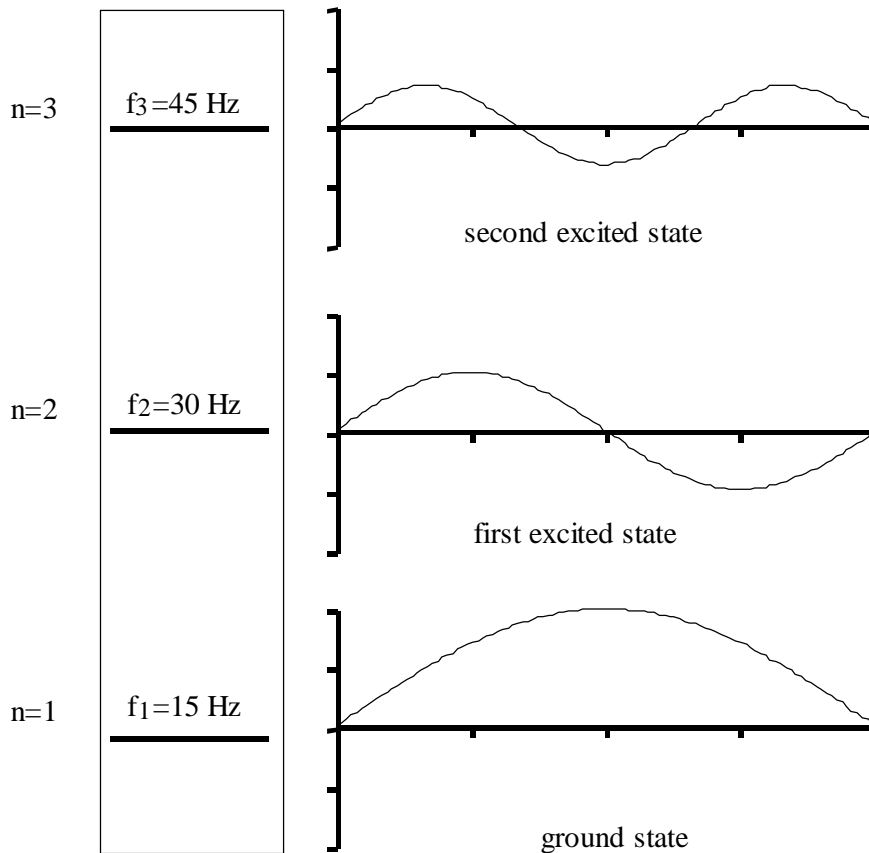
1.2 Standing waves with strings of non-homogeneous mass distribution

**Non-homogenous** mass distribution means that the <u>mass density</u> of the string is not the same over the entire length. The string is – in simple words – at some positions heavier than at others. As a result of this one could expect that the sting shows different Eigen-frequencies and amplitude functions for standing waves. As an example we use a string of the length of 0.53 m that has a mass density of 0.78 g/m for the first 0.38 m (only string), and 8.0 g/m for the remaining 0.15 m (string plus beads).
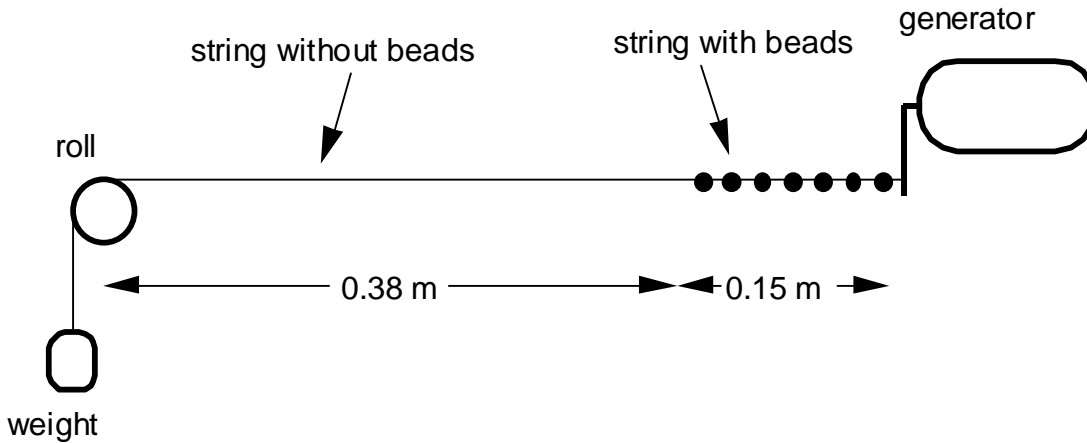
As a result of the weight hanging off the sting at the left end we find a constant tension over the entire string. On the right side the string is connected to a generator which can move up and down with adjustable frequency to stimulate the string to oscillate. The first three states of this experiment are shown in the picture below.

<u>state number n</u>	<u>Eigen-frequency f_n</u>	<u>amplitude function $y_n(x)$</u>
n=3	$f_3 = 27$ Hz	second excited state
n=2	$f_2 = 20$ Hz	first excited state
n=1	$f_1 = 8.6$ Hz	ground state

The amplitude functions shown in the picture are real photos, the frequencies have been measured. Because of the <u>non-homogeneous</u> mass distribution the frequencies do not show constant ratios (as did the frequencies of the standing waves with the <u>homogeneous</u> string which were $f_1=15$ Hz, $f_2=30$ Hz, $f_3=45$ Hz) and the shape of the amplitude functions has changed. One can see that the positions of the nodes are shifted to the side where we can find the higher mass density. Furthermore the **curvature** of the string is larger in the area of higher mass density. From the curvature of the amplitude function one can tell where the area of higher mass distribution is.

1.3 Theoretical description of standing waves

To understand how we can <u>calculate</u> the amplitude function of standing waves we need an understanding of **differential equations**. In the differential equations for standing waves we find the second derivative of the amplitude function, called y"(x). The amplitude function itself is called y(x). We want to give an example that explains y"(x) as the change of the slope or the curvature of the function y(x).
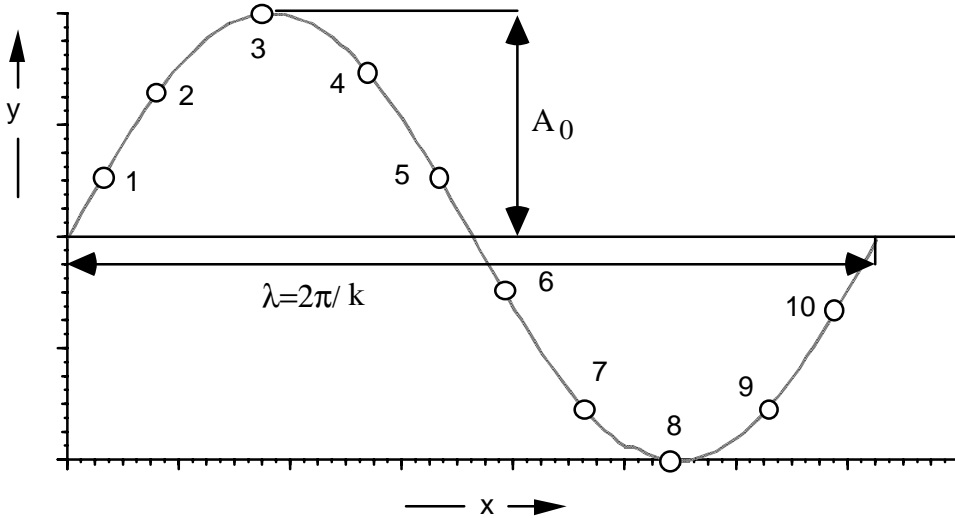
The curvature can be understood as the bending of the function. When you drive along a straight road with a car, the curvature is zero (between point 1 and 2 in the graph). When the road bends, the curvature is not equal to zero (from point 2 to 4 in the graph). The highest curvature is at the point 3. Between the points 5 and 6 the curvature is zero again (the line does not bend).

The graph shows a sine function (the amplitude function of a standing wave with homogeneous mass distribution). This function can be expressed in the following way:

$$y(x) = A_0 . \sin(k.x) \dots\dots\dots\dots\dots\dots\dots (1)$$

A_0 is the amplitude and k the wave number. These two constants define the amplitude function. When we differentiate this function twice we get:

$$y'(x) = A_0 . k . \cos(k.x) \dots\dots\dots\dots\dots\dots (2)$$

$$y''(x) = -A_0 . k^2 . \sin(k.x) \dots\dots\dots\dots\dots (3)$$

When $A_0 . \sin(k.x) = y(x)$ from equation (1) is put into equation (3) we get:

$$y''(x) = -k^2 . y(x) \dots\dots\dots\dots\dots\dots\dots (4)$$

The solution of this differential equation is the function (1) which we have put in to get the equation. Equation (4) shows the relationship between the amplitude function y(x) and its curvature y"(x). The greater the amplitude y(x) the greater the curvature y"(x) which can also be seen from the graph. Between the position 5 and 6 the amplitude is small and the function is straight. At the position 3 the amplitude is great and the function is bent.

With **k=2π/λ** (the relationship between the wave number k and the wave length λ) and **λ=c/f** (the relationship between the wavelength λ and the frequency f, c is the velocity of the wave in the string) the equation (4) can also be written as:

$$y''(x) = -\frac{4\pi^2 f^2}{c^2} . y(x) \dots\dots\dots\dots\dots\dots (5)$$

In the experiment we have shown in the previous section (1.2), the velocity c of the wave in the string depends on the tension F_s (from the weight) and the mass density m_s (mass per unit length) in the following way: **c²=Fs/ms**
When we put this relationship into equation (5) we get:

$$y''(x) = -4\pi^2 . f^2 . \frac{m_s(x)}{F_s} . y(x) \dots\dots\dots\dots\dots (6)$$

This equation is true even for a non-homogeneous mass distribution. The mass density m_s does not have to be constant. It can be written as $m_s(x)$ which means that the density varies with the position x.
Equation (6) shows the relationship between the curvature y"(x), the amplitude function y(x), and the mass density $m_s(x)$. Since $m_s(x)$ is multiplied with y(x) we find a great curvature at areas with higher mass density. We came to the same result when we observed the photos of the real experiment (see section 1.2).

1.4 Modeling standing waves with STELLA

STELLA is a software package which helps us solve differential equations. The equation is represented by graphical objects. Each object stands for a quantity in the equation. These objects have to be connected with arrows that show how the quantities relate to each other.

We are going to use STELLA to reduce the mathematical difficulties to solve the differential equation of standing waves with non-homogeneous mass distribution. From the model we also get the Eigen-frequencies of the standing waves.

In the model, all quantities from equation (6) can be found. **y** is the amplitude function, **y'** its first derivative and **y"** its second derivative. $\mathbf{F_s}$ is the force of the weight attached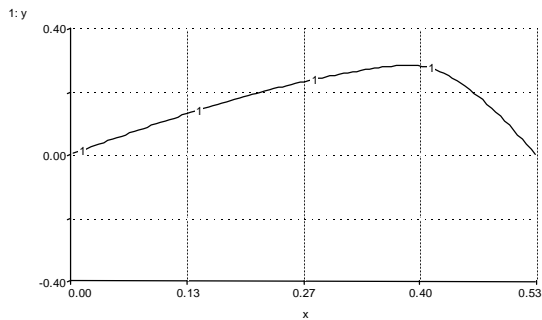 to the string (i.e. the tension in the string), **f** the frequency, and $\mathbf{m_s}$ the mass density depending on the position **x**.

We have to enter the values for $\mathbf{F_s}$, **f**, and $\mathbf{m_s}$ and the initial values for **y** (must be zero because the amplitude function starts with a node) and **y'** (can be any value except zero because the amplitude function starts with a slope not equal zero). y' and y'# are both the first derivative of y. The equation for y'# is just **y'# = y'**. The equation for the curvature y" is our differential equation (6). STELLA always names the x-variable TIME although in this model the x-axis is the position. Therefore we need an object for the position x with the equation **x = TIME**.

How does STELLA calculate the differential equation? In the example graph below STELLA starts at x = 0, ends at x = 0.5, and calculates only five steps (Δx=0.1). It start with the initial values we have to put in for y and y' (in this example y(x=0)=0 and y'(x=0)=1). In the graph this is position 1. It draws the first step (from position 1 to position 2) with the slope y' = 1. At the position 2, a the new amplitude y can be calculated (y(x=0.1) = 0.10, see also table). This is the input for the differential equation (6) and y" and y' can be calculated at the position 2. Then it draws the next step from position 2 to position 3 and so on. The table below shows the calculated values for y, y' and y" for the six positions.

x	y	y'	y"
0.0	0.00	1.00	-0.90
0.1	0.10	0.91	-2.54
0.2	0.18	0.66	-3.72
0.3	0.22	0.28	-10.74
0.4	0.23	-0.79	-23.60
0.5	0.00	-3.15	

When we use STELLA we normally cannot see the single steps because they are chosen to be very small and the graph looks like a continuous line. In this example the input for the mass density of the string was the same as the string in section 1.2 (0.78 g/m for the first 0.38 m (only string), and 8.0 g/m for the remaining 0.15 m (string plus beads)). At the positions 1 to 4 the we find a low mass density and the curvature (the change of the slope) is small. At position 5 the string has a high mass density and we can see from the graph that the slope changes greatly. We came to the same result from the observation of the experiment (section 1.2) and the theoretical discussion of the differential equation (section 1.3).

STELLA and Physics units. Because STELLA does not use units with the quantities we have to make sure all units on the left side equal out with the units on the right side. When we use SI-units we can be sure that they equal out.

Units on the left side:
$$\left[\frac{d^2 y(x)}{dx^2}\right] = \frac{M}{M^2} = \frac{1}{M}$$

Units on the right side:
$$\left[f^2 .m_s(x)\frac{1}{F_s}.y(x)\right] = \frac{1}{s^2}.\frac{kg}{M}.\frac{s^2}{kg.M}.M = \frac{1}{M}$$

E.g. when we use g/m for m_s instead of kg/m we have to multiply the right side of the equation by 10^{-3}.

$$\frac{g}{M} = 10^{-3}\frac{kg}{M}$$

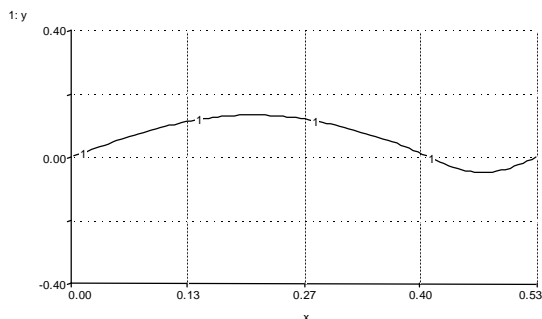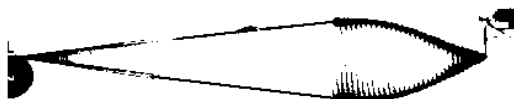## 1.5 Finding the amplitude functions with STELLA
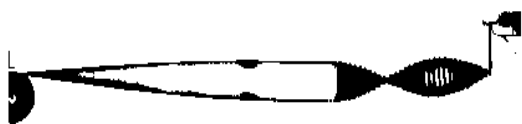

y(x) calculated with STELLA (f = 5 Hz)

y(x) calculated with STELLA (f = 10 Hz)

y(x) calculated with STELLA (f = 8.6 Hz)

To find the Eigen-frequencies and the amplitude functions of standing waves, we have to vary the frequency until the amplitude function fulfills the **boundary conditions**. This can be best shown in the following example:

The amplitude function has to have a node at the beginning (at x = 0.00 m) and the end (at x = 0.53 m) because in the real experiment the string cannot move at those positions. The boundary condition for the starting point is fulfilled with the initial value of y(x=0)=0. The graph on the left shows the amplitude function for the frequency f = 5 Hz. The graph does not come down to zero at x = 0.53 m and therefore this cannot be the amplitude function of a standing wave.

The second graph is the amplitude function for f = 10 Hz. Again, is does not end at zero and is therefore no solution of a standing wave. It can be seen from the two pictures that the frequency we are looking for is between 5 Hz and 10 Hz because the first graph ends above the x-axis and the second below the x-axis.

The third graph shows the amplitude function for f = 8.6 Hz. It fulfills the boundary conditions and is a solution for a standing wave. The solution matches with the photo from the experiment (shown below the graph). For the first three states the following table compares the experimental frequency with the result from the STELLA model:

state n=1: f = 8.6 Hz (experiment) f = 8.6 Hz (STELLA)
state n=2: f = 20 Hz (experiment)   f = 19.5 Hz (STELLA)
state n=3: f =27Hz (experiment)   f = 26.0 Hz (STELLA)

The STELLA values deviate a little from the experimental frequencies which is due to inaccuracies in the measurements.

y(x) calculated with STELLA (f = 19.5 Hz)

y(x) calculated with STELLA (f = 26 Hz)

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1.6 Description of bound electrons using "states"

Up until now we have used the term **state** with classical systems like standing waves. We have deduced the conditions of a standing wave from observing an experiment and have defined the Physics terms state, state number, Eigen-frequency, amplitude function and node. The theoretical description has been put into a STELLA model to solve the differential equation that describes standing waves. A comparison between the theoretical results and the experimental outcome has proved that the differential equation is able to predict the frequencies and amplitude functions of standing waves under the condition that the amplitude function has nodes at each end of the string.

Now, we ask what the description of standing waves has to do with electrons that are bound in atoms and how we can apply it to describe atoms. It has been found that:

- Electrons are bound in atoms in **discrete** states; these states can be numbered with state numbers like the states we have found with standing waves; in atomic Physics the state numbers are called **quantum numbers.**

- Each of these states is characterized by an Eigen-value. For standing waves this was the frequency, for bound electrons it is the **binding energy** of the electron. Therefore these energies are called **Eigen-energies**. Similar to the frequencies of standing waves we find only certain values of Eigen-energies (**discrete** Eigen-energies).

- The fundamental equation that describes bound electrons is a differential equation, called the **Schrödinger equation**. This equation has a very similar structure to the differential equation of standing waves. On the left side is the second derivative of a kind of amplitude function, called **distribution function** (**Ψ-function**, **Psi-function**), on the right side is the distribution function itself.

- The **distribution function** describes a bound electron and is <u>time independent</u> just like the amplitude function. It <u>cannot</u> be interpreted as the envelope of a motion but as the **charge distribution** of the electron (or **electron cloud**) around the nucleus.

Because atoms are three dimensional objects, a one dimensional description is a simplification of bound electrons. This simplification makes it possible to calculate the charge distribution in analogy to standing waves amplitude envelope. Similar to a level scheme for standing waves with state number, Eigen-frequency and amplitude function, an atom can be described graphically with a **level scheme** that contains the quantum numbers, Eigen-energies and distribution functions. The conditions for a distribution function are different from the conditions for standing waves. It starts at a radius r = 0 with a certain value and has to approach the r-axis asymptotically for large radii. There is no boundary the charge cloud is limited to. The first three states of the Hydrogen atom are displayed in the level scheme below.

| quantum number n	Eigen-energy E_n	distribution function $\Psi(r)$
n = 3	$E_3 = -1.5$ eV	
n = 2	$E_3 = -3.4$ eV	
n = 1	$E_3 = -13.6$ eV	

2. The Hydrogen atom

2.1 Models of the structure of atoms

Scattering experiment with atoms, carried out by Rutherford around 1904, showed that the positive charge and almost the entire mass of atoms is located in the center of the atom over a small volume. This center is called the **nucleus** or core of the atom which consists of protons (carrying the positive charge) and neutrons (not charged). During the last 100 years a variety of models have been developed on how the electrons (carrying the negative charge) are arranged around the nucleus. Atomic Physics deals mainly with the description of bound electrons. Three of the models are presented below.

A) The Bohr model

1913, Bohr formulated a decisive approach to describe atoms which explained experimental observations and contained an important step towards a quantum mechanical description of atoms. The experiments were mainly the scattering experiments from Rutherford and the observation of line spectra when an atomic gas is excited to emit light.

In a simple picture of this model, the electrons could be described as particles going around the nucleus quite similar to planets going around the sun. Because of the attraction between the opposite charges of the nucleus and the electrons, the electrons move in stable orbits. This motion is illustrated in the two dimensional picture below.
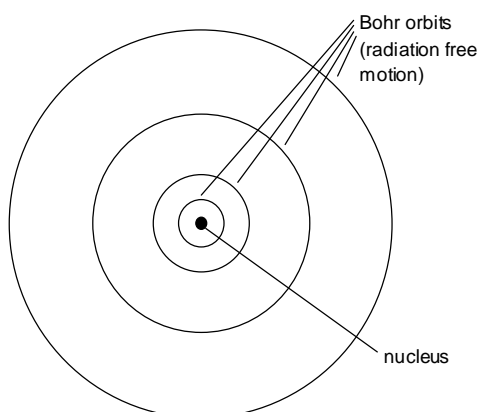
Limitations of the Bohr model:

The described motion would be possible for orbits of any radius and would therefore allow continuous distances between the nucleus and the orbit. When an atom emits energy in the form of light, the radius of the orbit is reduced. The amount of the emitted energy defines the frequency of the emitted light Therefore the light radiated from an atomic gas should show a continuous spectrum. Quite in contrast, one observes only light of certain frequencies (called **line spectrum**). The conclusion of this observation must be that the electrons move in orbits with discrete radii (called **Bohr orbits**, shown in the picture). All other orbits are forbidden. Because this observation violates the laws of classical mechanics, Bohr postulated these orbits although in contradiction with classical mechanics.

A second postulate emerges from Electro-dynamics. Electrons orbiting the nucleus should constantly emit energy. This would lead to a constantly decreasing distance between the electron and the nucleus and finally the electron would collapse into the nucleus. Because this behavior is not observed (atoms are stable), Bohr had to postulate radiation free orbits in contradiction to Electro-dynamics. The electrons moving in Bohr orbits do not radiate.

That this description of atoms cannot be satisfying lies in the formulation of postulates. The classical Physics has been extended by these demands which are only valid for electrons but not for macroscopic objects (e.g. a billiard ball). Nevertheless these postulates were an important step towards a development of a new theory.

B) A quantum mechanical description of bound electrons

When an electron is no longer treated as a classical object but as a **quantum object** (like in the electron double slit experiment, Serway chapter 41.3), we come to the following description:

The electron is described with a distribution function called Psi-function (Greek letter Ψ). This function has a certain value for each position around the nucleus and is calculated with the Schrödinger equation, the fundamental equation in atomic physics which we are going to discuss in detail later. One of its results is the discrete energy states which had to been postulated in the Bohr model. With this result the Schrödinger equation is able to explain the line spectrum of a radiating atom. Because we cannot speak about motion or orbits any more, but only about states when we talk about bound electrons, we do no longer need the second Bohr postulate for radiation free orbits. The advantage of this new description is that it is not based on postulates.

Unfortunately the theory around the Schrödinger equation and the Psi-function contains a disadvantage which led to continuing discussions among physicists until today. The distribution function which describes the electron

around the nucleus does not allow a simple picture of an electron as a classical particle as described in the Bohr model. There are a variety of interpretations of the Psi-function. Two are collected here:

Interpretation I (localization probability):

Max Born (1926), physicist

I would like to give an interpretation (of the Psi-function). I want to refer to a remark from Einstein about the relationship between the wave field and the light quanta. He said that the only purpose of the waves is to lead the way for the light quanta and therefore he spoke about a "ghost field". This field defines the probability of a light quantum, the carrier of energy and momentum, to follow a certain path. The field itself does not carry any energy or momentum.
When one draws the complete analogy between light quanta and electrons, the laws of the electron motion have to be formulated in a similar way. It is obvious that the Broglie-Schrödinger waves are seen as the "ghost field" or better the "leading field".
The paths of these particles are only defined as far as the conservation of energy and momentum limit them. We can only give a probability for a particle to follow a certain path which is defined by the values of the Ψ-function.

In the text, Born is referring to the interpretation of the localization probability in the double slit experiment with electrons. The experiment shows the same interference pattern as the double slit experiment with light. When you localize (measure the position of) an electron on the screen behind the double slit you can only give a probability to find an electron at a certain position. The probability is given by the Psi-function.
When we apply these ideas on bound electrons we could interpret the Psi-function in the following way:
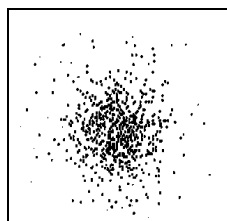
- The picture on the left shows the result from a few hounded localization measurements of the electron. It is more probable to find the electron close to the nucleus than further away from the nucleus.
- The probability to localize an electron in a small volume ΔV is $\Psi^2 * \Delta V$. This means that you have to multiply Psi squared at a certain radius by the volume ΔV to calculate the probability to find the electron in the volume ΔV.

Interpretation II (charge cloud):

Friedrich Hermann (1990), developed a physics course for High School students (year 8 and 9)

The electron is an extended object. Its form is described through its distribution function. Therefore the form depends on the state the electron is in. To describe an electron like that, we need a name for something which does not exist in a traditional model: a name for this matter, electrons consist of. We have called this matter Electronium.
*The introduction of this name makes it easier to describe the structure of atoms: the atom consists of a small heavy nucleus and a large light cloud. The cloud consists of Electronium which has a high density in the center. The density decreases constantly with increasing radius. There is no sharp boundary. When one tries to take away a part of the Electronium it can be observed that one can only get a certain portion: a certain amount of Electronium. We call this elementary amount an electron.*
In states of the atom which are called Eigen-states of the energy, the distribution and therefore the form of the Electronium is constant in time: the Electronium does not move.
We think that this description of electrons is nothing new in principle. Physicists, Chemists and Crystallographs have been working with this model all the time. Instead of Electronium they talk about orbitals or electron density distribution. What is missing is a name for the matter they are talking about: Electronium.

The interpretation, Hermann is giving about the Psi-function is originally designed for High School students of year 8 and 9. Nevertheless it provides a picture of the Psi-function which is easy to understand and is close to an interpretation from Schrödinger who pictured the electron as a cloud around the nucleus.
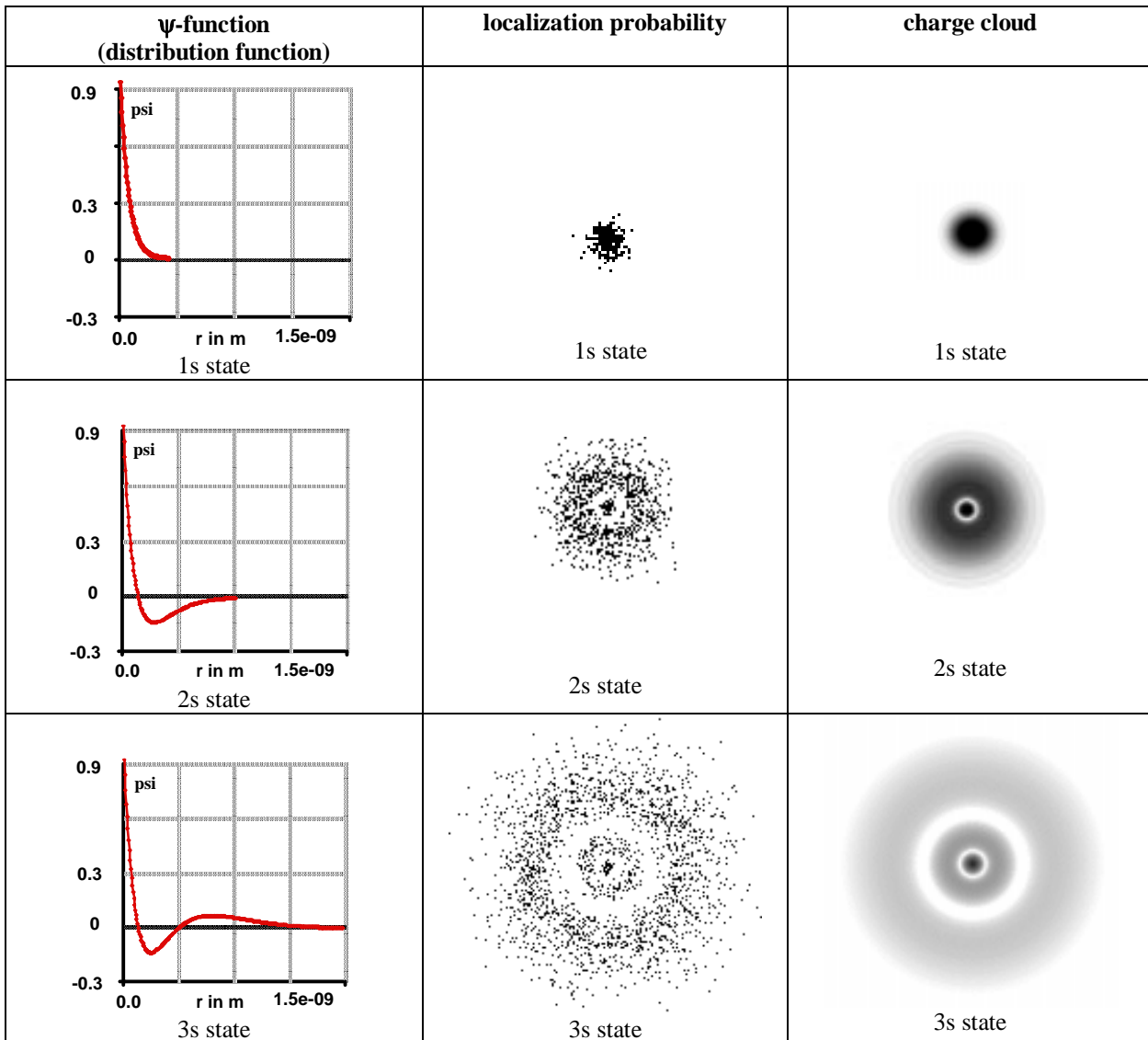When we apply these ideas on bound electrons we could interpret the Psi-function in the following way:
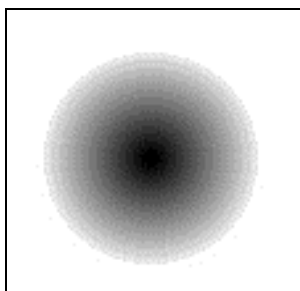
- The picture on the left shows a charge cloud of one electron around the nucleus. The charge cloud is spread out over a large volume compared to the nucleus.
- $e*\Psi^2*\Delta V$ is the part of the electron charge in the volume ΔV. This means that you have to multiply the elementary charge e by Psi squared at a certain radius by the volume ΔV to calculate the charge that you find in the volume ΔV.

2.2 States of bound electrons

Our first aim is to find the equation to calculate the states (distribution functions and Eigen-energies) of bound electrons. In classical physics the description of a particle in an orbit (e.g. the orbit of a planet around the Sun) can be calculated to predict its position at any time. In atomic physics we calculate a state, characterized by its distribution function and Eigen-energy. Two possible interpretations of the distribution function have been given in the last section. When we talk about states, we cannot use the terms "orbit" and "motion" any more. They are replaced by the distribution of the electron around the nucleus. At positions where the Psi-function has a large value it is more likely to localize an electron than at positions where the Psi-function has a small value (interpretation of localization probability). At positions where the Psi-function has a large value the charge density is higher than at positions where the Psi-function has a small value (interpretation of charge cloud). The following picture shows the first three states of the Hydrogen atom in three interpretations.

ψ-function (distribution function)	localization probability	charge cloud
1s state	1s state	1s state
2s state	2s state	2s state
3s state	3s state	3s state

On the left side the Psi-functions or distribution functions are shown. This is the most abstract representation: the functions give certain values for any radius. It can be seen that the Psi-functions of the first and second excited states (2s and 3s) show nodes: at these positions the function is zero.

The pictures in the middle show the interpretation of the localization probability. Each point represents the measurement of the position of the electron. When we measure the position of the electron many times we get one of these pictures depending on the state the atom is in. These pictures are only two dimensional (the third dimension gives a spherical symmetric picture of the atom). Psi squared (Ψ^2) is directly related to this picture: at positions where Ψ^2 is large it is more probable to localize the electron than at positions where Ψ^2 has a small value. At the nodes the electron can never been found: the localization probability is zero (2s state: one node, 3s state: two nodes).

The pictures on the right side show the interpretation of the charge cloud. They represent the charge distribution of the electron around the nucleus depending on the state the atom is in. Again, these pictures are only two dimensional. The third dimension would show a spherical symmetric charge cloud. Psi to the power of two (Ψ^2) is directly related to this picture: at positions where Ψ^2 is large the charge density is high. At the nodes the charge density is zero.
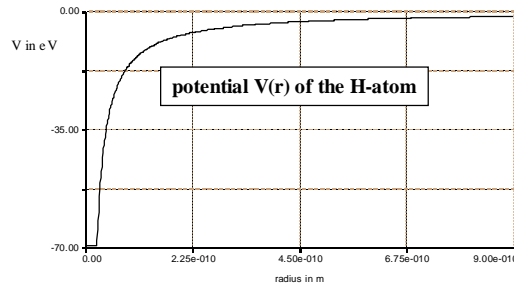
2.3 The Schrödinger equation

An equation that describes atoms has to contain all physical quantities of an atom. The equation for standing waves contained frequency, mass distribution, tension and amplitude function. What quantities would we expect in an equation to describe atoms:

-   **Binding energy**: we need a certain amount of energy to take away an electron from the atom (this is called ionization). The charge cloud is bound to the nucleus with a certain energy. By definition a free electron has a positive energy while a bound electron has a negative energy. The energy **E** of a bound electron has a negative sign. The energy values are analog to the frequency f of standing waves.
-   **Distribution function**: the equation should be able to calculate the distribution function of the charge cloud referring to the binding energy E. The distribution function is analog to the amplitude function of standing waves.
-   **Potential of the nucleus**: the interaction of the positive charged nucleus with the negative charge cloud has to be taken into account. The electrostatic force F(r) (7) between the nucleus (Hydrogen) and the charge cloud is equal to the first derivative of the potential multiplied by minus one (8). The potential is given by equation (9). The force and the potential depend on the distance r. The graph shows the potential of the Hydrogen atom.

$$F = -\frac{1}{4\pi\varepsilon_0} \cdot \frac{e^2}{r^2} \dots\dots\dots\dots(7)$$

$$-\frac{d}{dr}V(r) = F(r)\dots\dots\dots\dots(8)$$

$$V(r) = -\frac{1}{4\pi\varepsilon_0} \cdot \frac{e^2}{r}\dots\dots\dots\dots(9)$$

potential V(r) of the H-atom

e is the elementary charge (e = 1.60*10^{-19}C), **ε$_0$** a constant called the permeability of free space (ε$_0$ = 8.85*10^{-12}C^2/Nm^2).

$$u''(r) = -8\pi^2 \cdot \frac{m_e}{h^2} \cdot \big(E - V(r)\big) \cdot u(r) \dots\dots(10)$$

The differential equation (10) is the **Schrödinger equation**. It contains the energy E, the potential V(r), the **radial distribution function u(r)**, its second derivative **u''(r)** (u''(r) can be interpreted as the curvature of the function u(r)) and two constants: **m$_e$** is the electron mass (m$_e$ = 9.11*10^{-31} kg), **h** is called Planck's constant (h = 6.63*10^{-34}Js).

The Schrödinger equation is the fundamental equation of quantum mechanics. It has a quite similar structure to the differential equation of standing waves. Since the string is only an one dimensional object but atoms are three dimensional, the Schrödinger equations (10) can only calculate spherical symmetric states of the atom (this means that the charge density depends only on the radius). The radial distribution function u(r) is depending only on one variable (the radius r) although an atom extends in three dimensions.

To get the Psi-function (distribution function) from u(r) (radial distribution function) we have to use equation (11).

$$\Psi(r) = \frac{u(r)}{r} \dots\dots\dots\dots\dots\dots(11)$$

We want to summarize how to calculate the charge distribution (see diagrams below):

1. put in the potential **V(r)** of the nucleus into the Schrödinger equation (10)
2. solving the equation gives the Eigen-energy **E** and the radial distribution function **u(r)**
3. dividing the radial distribution function u(r) by r gives the distribution function **Ψ(r)**
4. **Ψ(r)^2** gives the charge density of the cloud around the nucleus
5. now we can draw Ψ(r)^2 in two dimensions to get the picture of the **charge cloud**

1. potential V(r)

2. radial distribution function u(r)

3. distribution function Ψ(r)

4. distribution function squared Ψ(r)^2
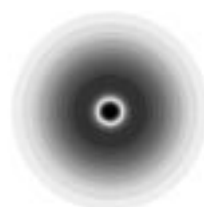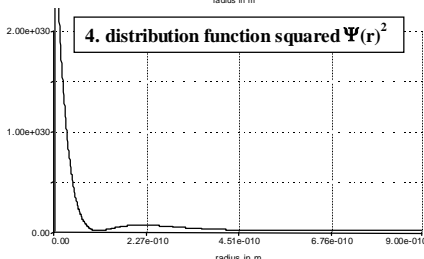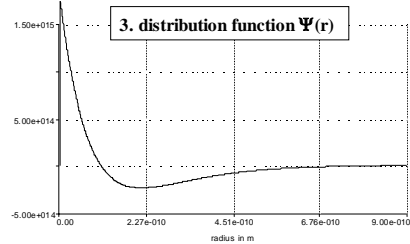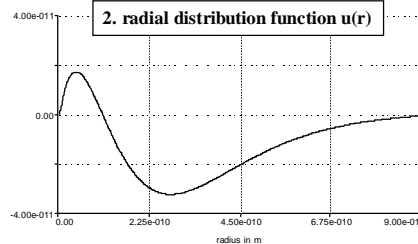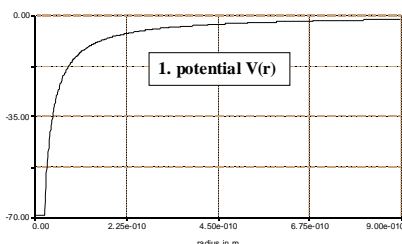
5. picture of the charge cloud

2.4 Modeling the Hydrogen atom with STELLA

Because we cannot solve the Schrödinger equation analytically (a second order differential equation) as we could not solve the differential equation of standing waves, we let STELLA do the work for us. For this purpose we need a STELLA model (it is very similar to the model of standing waves).
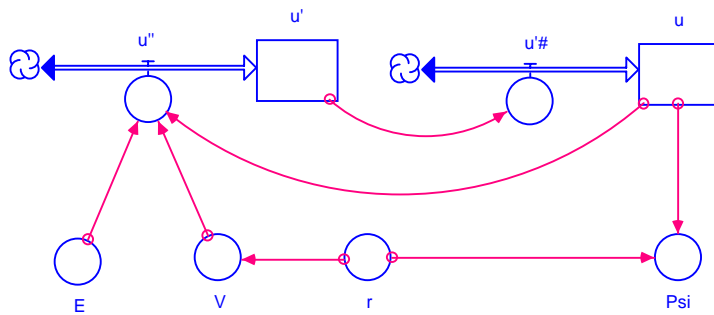
The model on the left contains all quantities of the equation (10): energy E, potential V, radial distribution function u(r) and its second derivative u"(r). To objects have been added. r = TIME (the radius) and Psi = u/r (definition of the Psi-function).

We could put in the constants described in the Schrödinger equation and the potential in SI-units and let the model run, but since quantities in atomic physics are very small, we might use units other than SI-units. The size of an atom is around 10^{-9}m which is called **nano-meter** (**nm**). A very common unit for the energy is the **Electron-volt** (**eV**) which is $1.60*10^{-19}$J = 1eV.

We calculate the constants in the Schrödinger equation and the potential first and put these values in the model. Since STELLA calculates without units we have to make sure that all units on the left side of the equation cancel out with the units on the right side. For this reason we write all values in nm and eV. You don't have to go through the entire calculation. The results are given in equations (12) and (13):

$$8\pi^2 \frac{m_e}{h^2} = 8\pi^2 \frac{9.11 \cdot 10^{-31} kg}{(6.63 \cdot 10^{-34} J \cdot s)^2} = 8\pi^2 \frac{9.11 \cdot 10^{-31} kg \cdot s^2}{(6.63 \cdot 10^{-34} kg \cdot m^2 \cdot s) \cdot (6.63 \cdot 10^{-34} J \cdot s)} = 16.3 \cdot 10^{37} \frac{1}{J \cdot m^2} = 16.3 \cdot 10^{37} \frac{1}{6.24 \cdot 10^{18} eV \cdot 10^{18} nm^2} = 26.3 \frac{1}{eV \cdot nm}$$

$$8\pi^2 \frac{m_e}{h^2} = 26.3 \frac{1}{eV \cdot nm^2} \quad ....(12)$$

$$\frac{e^2}{4\pi\varepsilon_0} = e \cdot \frac{1.60 \cdot 10^{-19} C \cdot N \cdot m^2}{4\pi \cdot 8.85 \cdot 10^{-12} C^2} = e \cdot 1.44 \cdot 10^{-9} \frac{V \cdot C \cdot m}{C} = 1.44 \cdot 10^{-9} eV \cdot m = 1.44 eV \cdot nm$$

$$\frac{e^2}{4\pi\varepsilon_0} = 1.44 eV \cdot nm ....(13)$$

With these calculations we can write the Schrödinger equation (10):

$$u''(r) = -26.3 \cdot (E - V(r)) \cdot u(r) \quad \text{with} \quad V(r) = -\frac{1.44}{r}$$

This is the input for the STELLA model. The starting value for radial distribution functions u(r) is zero, the slope can be any value except zero (e.g. 1). In the Time Specs menu we have to put in the values for the radius. Start at a very small value (e.g. 10^{-6}nm; not zero because this would give a division by zero in the potential) and go up to 0.5 nano-meter. Now we can try some energy values to find the states of the Hydrogen atom. How this is done is explained in detail in the next chapter.

2.5 Finding the states of the Hydrogen atom with STELLA

E = -15eV
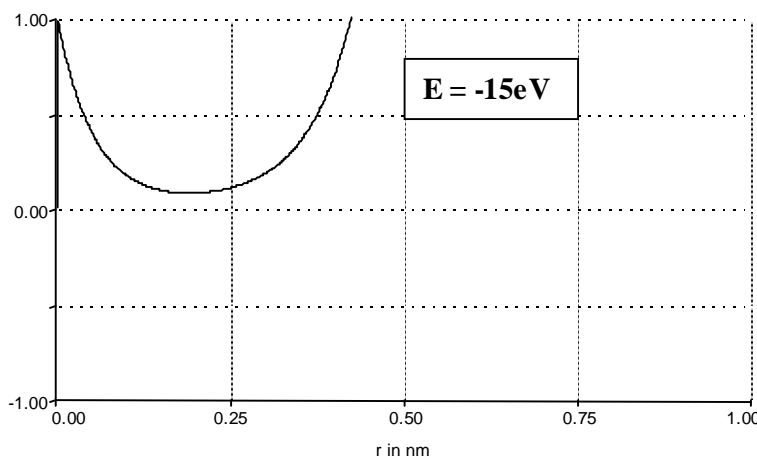
Until now we have presented various models and interpretations to describe the Hydrogen atom. Let us try to calculate the first states of the Hydrogen atom with the STELLA model that has been presented in the last section and which is based on the Schrödinger equation. We start with an energy value of E = -15eV. The first graph on the left shows what the Psi-function for this energy looks like.

We already know that Psi squared gives the charge distribution of the electron around the nucleus. For large radii this function should go to zero. This boundary condition is similar to the boundary condition of standing waves which had a node at both sides of the amplitude function because the string could

E = -10eV

E = -13.6eV

r in nm

E = -5eV

E = -3eV

r in nm

E = -3.4eV

r in nm
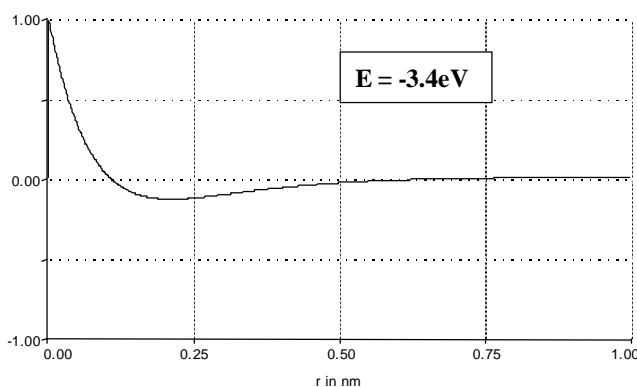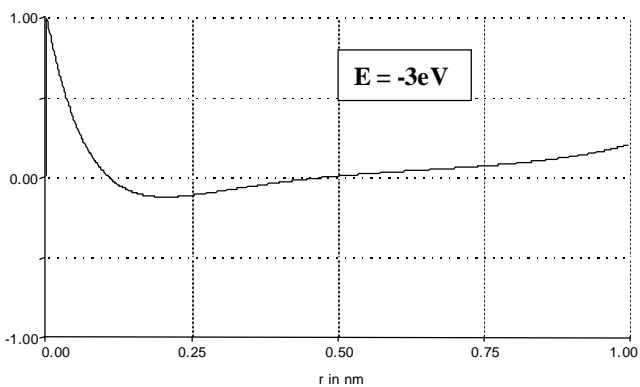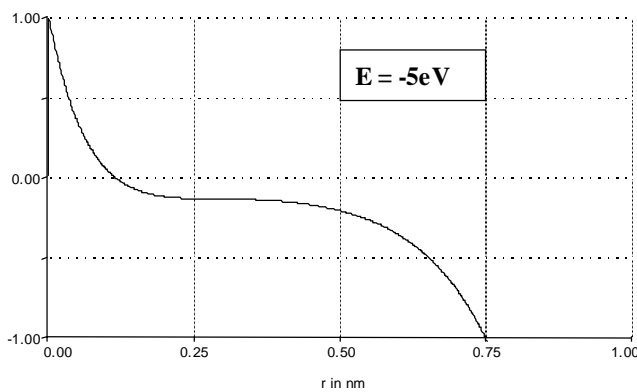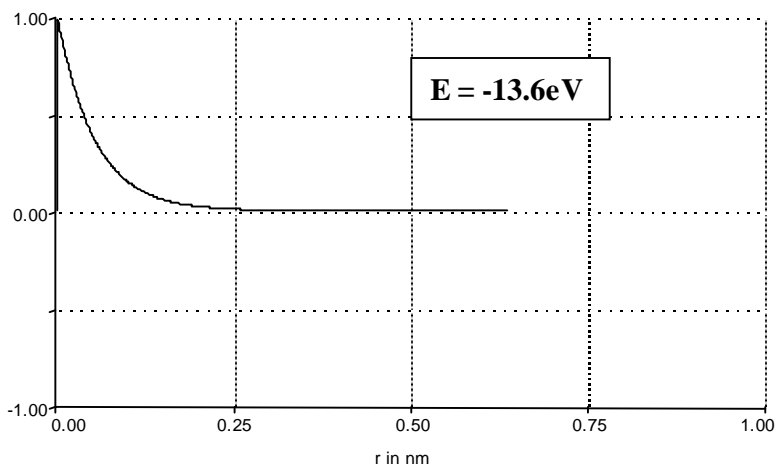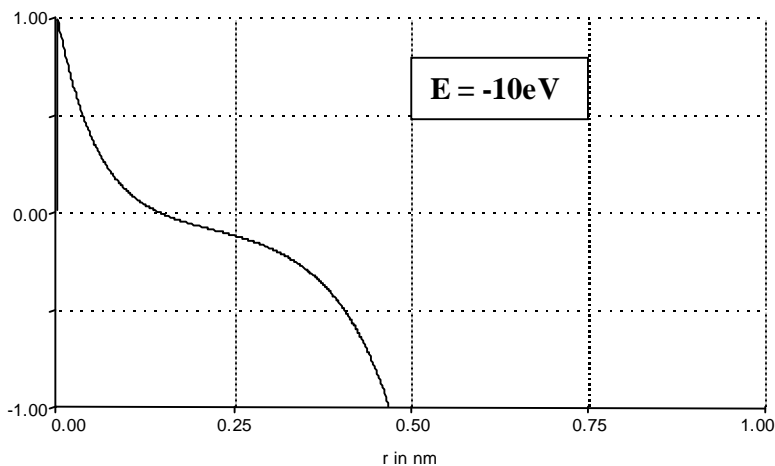
not move up and down at those positions. For atoms the Psi-function represents the charge density which is large at the nucleus and goes asymptotically to zero for large radii.

For this reason the first graph cannot be a state of the Hydrogen atom. The Psi-function and therefore also the charge density increases drastically with large radii. This is in contradiction with bound electrons.

Let us try an energy value of E = -10eV. The graph shows one node (at about r = 0.15nm) and goes drastically down for large radii. For the same reason as the first graph does not represent a state of the Hydrogen atom, this graph does not show a state either. Because the first graph did not have a node but the second had one, we can predict that the ground state of the hydrogen atom must be between –15eV and –10eV.

After a few tries one finds the state at around E = -13.6eV. The Psi-function of the state called 1s is shown on the left. It constantly increases its value and goes asymptotically to zero. We have seen the picture of the charge cloud and the localization probability of the 1s state on page 10.
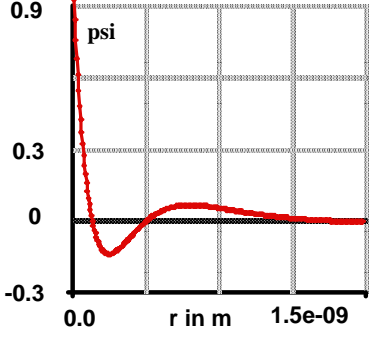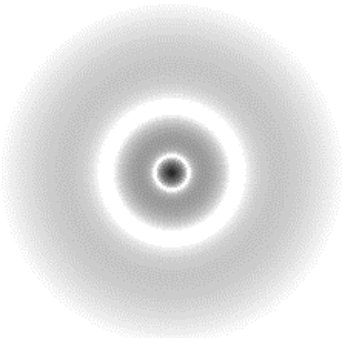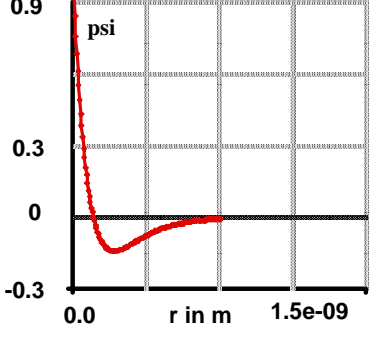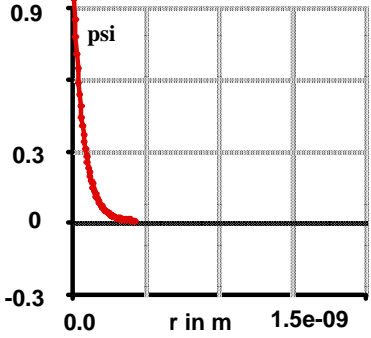
The same procedure can be done to find the 2s state (the first excited state) of the Hydrogen atom. The next three graphs show the Psi-functions for E = -5eV, E = - 3eV and E = -3.4eV.

It can be seen that the Psi-function for E = -5eV has only one node but does not go to zero for large radii. Neither does the Psi-function for E = -3eV which has two nodes. The energy of the 2s state has to be between these two values. It is found around E = -3.4eV. The graph on the left shows a Psi-function with one node. The function goes to zero asymptotically. It fulfills the boundary condition and is therefore the second state (first excited state).

One could ask the question if there are other states between 1s and 2s. This can be answered with no; no graph between E = -13.6eV and E = -3.4eV comes back to the r-axis after the first node. They all "fall down" to very large neg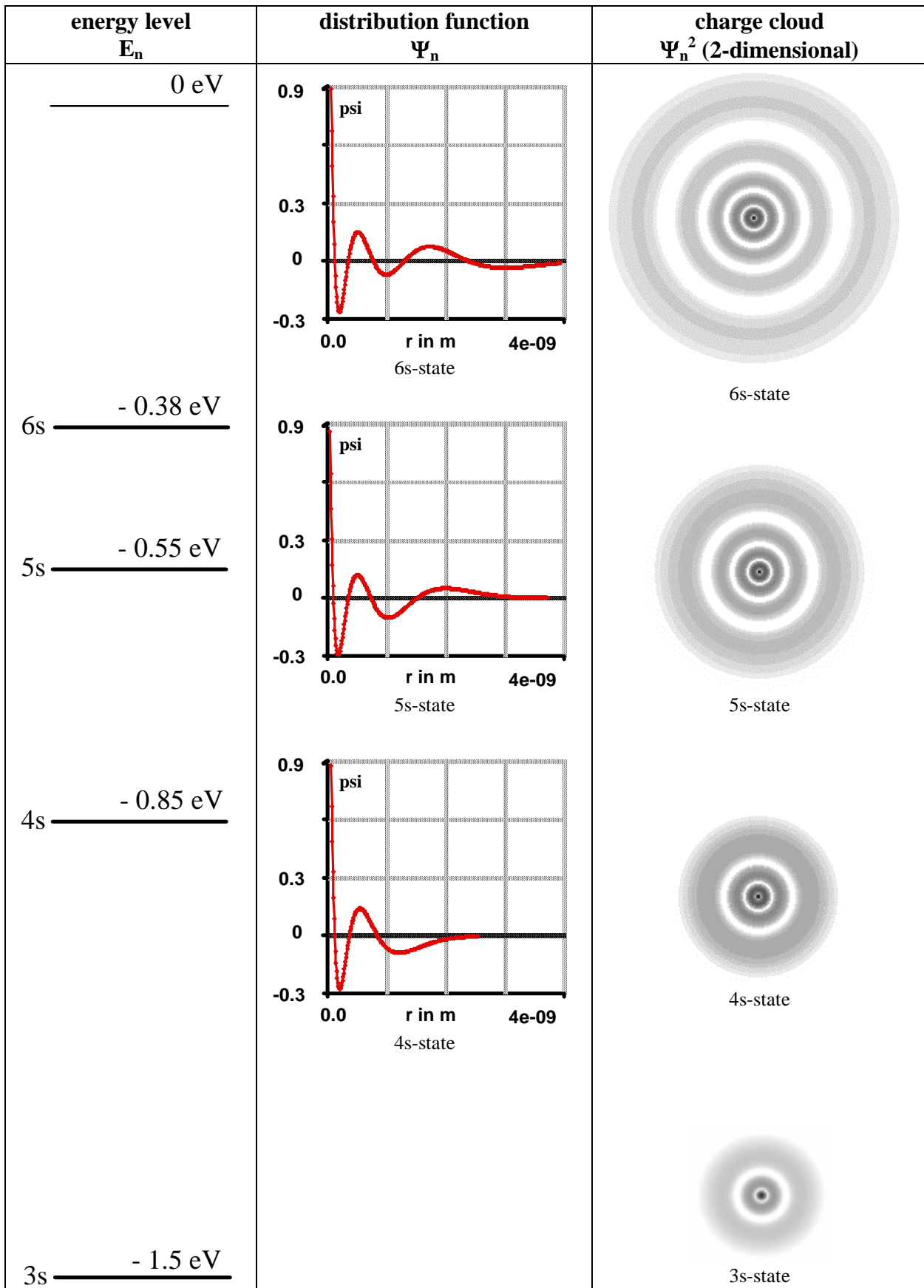ative values for large radii. Because of the interpretation of Psi square as the charge distribution these graphs do not represent a state. There are no other states between 1s and 2s. One could also ask the question why there is a lowest state (the 1s state). All graphs with energies lower than E = -13.6eV have a graph with no node which "goes up" without reaching the r-axis. These graphs are no states of the Hydrogen atom. These observations are analog to the description of standing waves.

Results from STELLA calculations of the Hydrogen atom
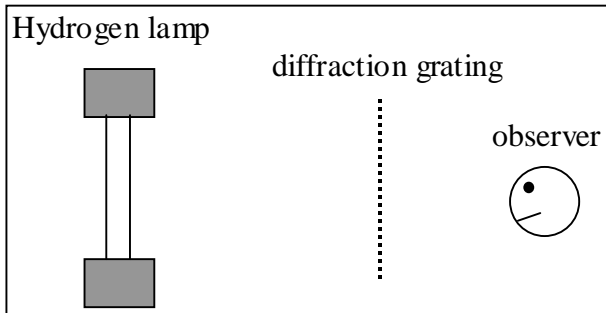
(first three states)

energy level E_n	distribution function Ψ_n	charge cloud Ψ_n^2 (2-dimensional)
0 eV	3s-state	3s-state
3s – 1.5 eV	2s-state	2s-state
2s – 3.4 eV		
	1s-state	1s-state
1s – 13.6 eV		

Results from STELLA calculations of the Hydrogen atom

(states 4s, 5s and 6s; the 3s state is shown only for comparison; the energy scale on the left starts at –1.5 eV)

energy level E_n	distribution function Ψ_n	charge cloud Ψ_n^2 (2-dimensional)
0 eV	6s-state	6s-state
6s — - 0.38 eV	5s-state	5s-state
5s — - 0.55 eV	4s-state	4s-state
4s — - 0.85 eV		
3s — - 1.5 eV		3s-state

2.6 The Hydrogen spectrum

Hydrogen lamp

diffraction grating

observer

How is a Hydrogen spectrum produced?
In a Hydrogen lamp an atomic gas of Hydrogen is produced (at room temperature Hydrogen is in the form of molecules H_2) and the atoms are excited via collisions with electrons. When the H-atoms fall back to lower states, electromagnetic radiation is emitted (visible light, ultraviolet light, infrared light). The light of the Hydrogen lamp can be split into its frequencies (or wavelengths) with a diffraction grating. Behind the grating the observer can see the spectrum.

line spectrum of Hydrogen

violet   blue   green-blue   red
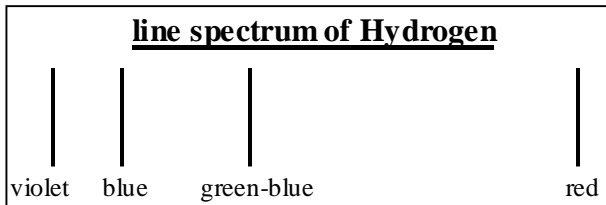
| color	wave length λ	frequency f	photon energy h*f
red	656 nm	457 THz	1,89 eV
green-blue	486 nm	617 THz	2,55 eV
blue	434 nm	691 THz	2,86 eV
violet	410 nm	731 THz	3,02 eV

The Visible Spectrum
With the help of the diffraction grating one can observe the frequencies of the light emitted by the Hydrogen atoms. In contrast to the spectrum of a light bulb (which shows a **continuous spectrum**), the Hydrogen lamp emits only certain frequencies. We call this spectrum a **line spectrum**. The picture above shows the visible line spectrum of Hydrogen. Under good conditions four lines (red, green-blue, blue and violet) can be observed.

The table shows the wave length λ, the frequency **f** and the photon energy **h*f** of the four lines. The wave length is obtained from the experimental measurement, the frequency and the photon energy (see also photoelectric effect, Serway chapter 40.2) are calculated from the wave length.

$$f = c / \lambda \dots\dots\dots\dots\dots\dots\dots\dots\dots(14)$$

$$E = h \cdot f \dots\dots\dots\dots\dots\dots\dots\dots\dots(15)$$

c is the speed of light (c = $3.00*10^8$ m/s)
h is Planck's constant (h = $6.63*10^{-34}$ Js)
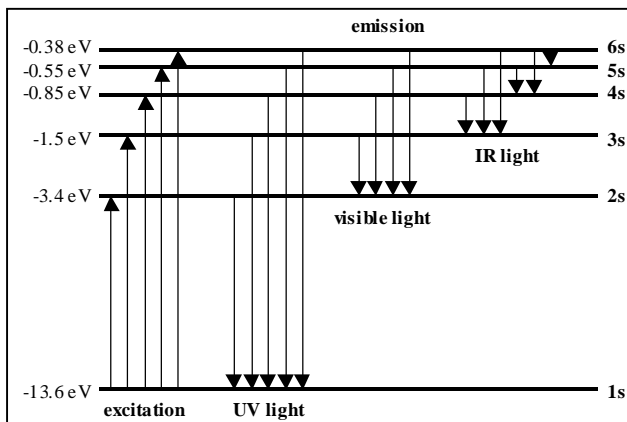
Explanation of the line spectrum
As we have seen with our STELLA calculations based on the Schrödinger equation, the Hydrogen atoms can only be in certain states. In each state the atom has a certain energy. We found the energy levels of the first six states of the Hydrogen atom to be:
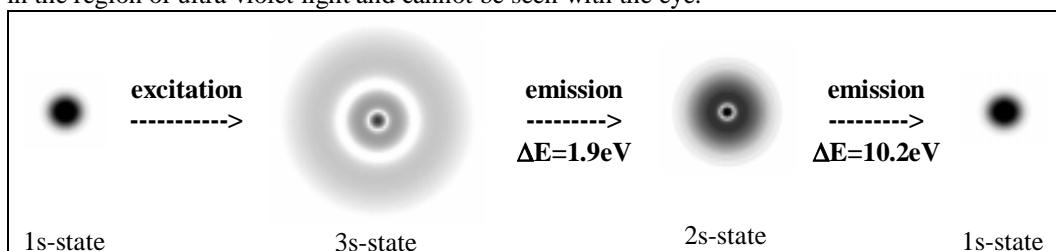E_1 = -13.6eV E_2 = -3.4eV E_3 = -1.5eV
E_4 = -0.85eV E_5 = -0.55eV E_6 = -0.38eV
When an atom is excited via an electron collision, its energy is increased and is goes from the ground state to an excited state ("**excitation**", arrows pointing upwards in the picture). When the atom goes from a higher state into a lower state ("**emission**", arrows pointing downwards in the picture), the atom emits a photon of the energy difference

between the two states **ΔE = h*f**. The emitted photons in the region between 1.5eV and 3eV correspond to frequencies of visible light. The transitions that emit visible light are the transitions from higher states to the 2s-state (called the Balmer series, see picture). When the energy difference between the two states is larger than 3eV the radiation is in the ultra violet region, when it is smaller than 1.5eV it is in the infra red region. This light cannot be seen by the eye.

The picture below shows an example of a possible excitation of Hydrogen. The atom is excited from the ground state to the 3s-state. When it goes down from 3s to 2s, it emits a photon of the energy ΔE= (-1.5eV) – (3.4eV) = 1.9eV. This energy is in the region of visible light. The transition is the red light emitted from the Hydrogen lamp. When the atom goes further down from 2s to 1s, the emitted photon has the energy ΔE= (-3.4eV) – (13.6eV) = 10.2eV. This energy is in the region of ultra violet light and cannot be seen with the eye.

excitation
---------->

emission
---------->
ΔE=1.9eV

emission
---------->
ΔE=10.2eV

1s-state   3s-state   2s-state   1s-state

2.7 Experiments to determine the size of atoms

We have seen from our calculations of the Psi-functions that atoms have no sharp boundary. The Psi-function approaches the r-axis asymptotically; for large radii the Psi-function is very small but not zero. In the picture of the localization probability this means that the electron can be found even at very large distances from the nucleus, but just with a very small probability. In the picture of the charge cloud this means that the charge cloud never ends. The charge density is just very small at large radii.
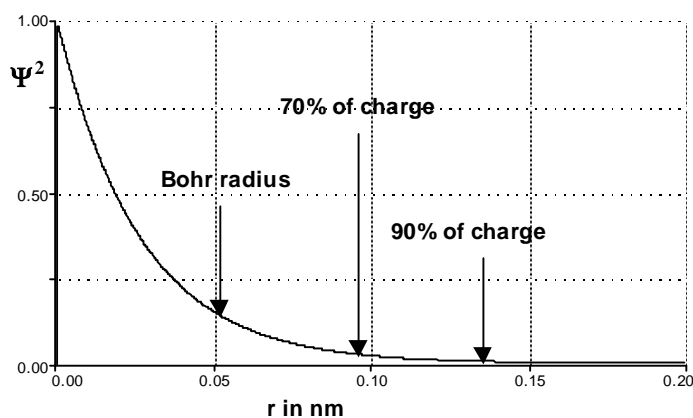

The graph shows the Psi square function of the Hydrogen atom in the ground state. The **Bohr radius** (r = 0.053nm) is the distance of the electron from the nucleus in the <u>Bohr model</u>. In the description of the Psi-function one can see that within this radius we find a high charge density, outside the charge density is quite low. Nevertheless the term "radius" is not very appropriate because the Psi-function does not go down to zero and the atom has no sharp boundary. In fact, in the picture of the localization probability it is more probable to find the electron outside the Bohr radius than within.

The graph shows two other possibilities to <u>define</u> the size of an atom. In the picture of the charge cloud we could define the radius at the distance where we find 70% (r = 0.095nm) or 90% (r = 0.14nm) of the charge inside a sphere with this radius. In the picture of the localization probability the probability to find the electron within the distance of 0.095nm from the nucleus would be 70% or within the distance of 0.14nm would be 90%.

Not only the <u>theoretical</u> value for the radius of atoms has to be defined; depending on the method of measurement we also find different atomic radii from experiments. Three <u>experimental</u> definitions of the radius of atoms are given here:

covalent bonding radius r = d/2
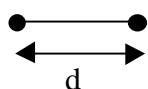
In a molecule (e.g. H_2) the two nuclei have a certain average distance **d**. The picture shows just the nuclei, the charge cloud has been left out to make the distance visible. The radius **r** of one Hydrogen atom is half the distance between the two nuclei. This radius is called the **covalent bonding radius**. It can be determined from emission spectra of the molecules.

volume, the atoms occupy in a gas, r = d/2
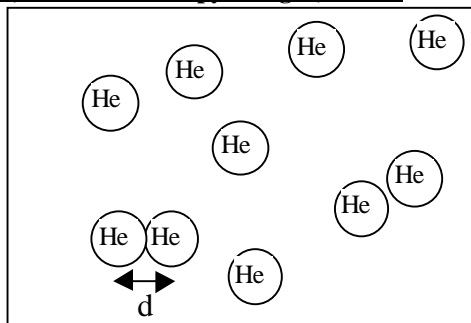
The atoms of a mono-atomic gas (e.g. Helium) occupy a certain amount of the space. This volume can be determined with van der Waals' equation (see Serway page 606). From the volume one can calculate the radius of the atoms.

**radius from ion bonds d = r_{Cl} + r_{Na}**
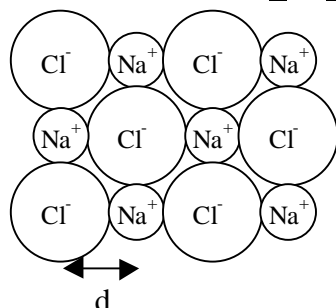
In crystals the ions (e.g. Na^+ and Cl^-) form a regular pattern or grid. The distance between two ions is just the sum of the radii of each ion. The distance can be determined with the method of diffraction of X-rays.

All these methods also have a disadvantage; they can only be applied on atoms or ions that make a particular bonding. At room temperature only noble gases are mono-atomic. Hydrogen forms molecules at room temperature. On the other hand Helium does not make covalent bonds. If we wants to compare the size of different atoms we have to use the same experimental method.

The tables below show measured and calculated atomic radii of Hydrogen, Helium, Lithium and the Lithium[+]-ion

	measured radii		
element	covalent bond	van der Waals	ion bond
H	0.032 nm	0.13 nm	-
He	-	0.11 nm	-
Li	0.15 nm	-	0.15 nm
Li$^+$	-	-	0.068 nm

	calculated radii	
element	70% of charge	90% of charge
H	0.093 nm	0.14 nm
He	0.045 nm	0.070 nm
Li	0.22 nm	0.30 nm
Li$^+$	0.030 nm	0.050 nm

3p
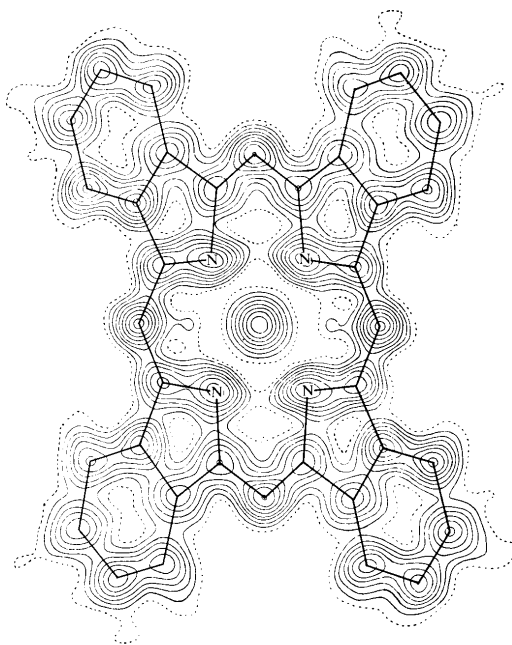
2.8 Can the charge cloud be measured?

With the method of X-ray diffraction which has been mentioned with ion bonding, it is possible to "take pictures" of charge clouds of even very complex molecules. For this kind of measurement it is necessary that the molecules form a crystal (regular pattern or grid). X-ray diffraction measurements are taken out under many different angles and finally it is possible to construct the picture from the diffraction patterns. The mathematical method to calculate the picture is rather complicated and shall not be mentioned here.

The picture shows the measured charge cloud of nickel-phthalocyanin. The circles show areas of the same charge density. The nuclei sit in the middle of each bunch of circles. The charge density decreases with the distance from the nucleus.

2.9 Non-symmetric states

All states we have calculated and discussed until now are **spherical symmetric**. The charge density depends only on the radius. We have called these states s-states (1s, 2s, ...). They could be distinguished by only one quantum number.

The limitation of spherical symmetric charge clouds are a result of the simplifications of the Schrödinger equation we have used in our STELLA model. It can only calculate the radial dependence of the Psi-functions. However, the Schrödinger equation for three dimensions can also calculate non-symmetric charge clouds like the one of the 3p-state pictured on the left. The picture shows the **orbital** (not to be mixed up with orbit!) of the electron in the 3p-state. In the picture of the localization probability the orbital can be interpreted as the space where it is most likely to find the electron. In the picture of the charge cloud the orbital shows the region of high charge density.

Although the 3p orbital consists of several areas which are separated by nodes, the picture shows the orbital of <u>one</u> electron. Also the higher s-states that we have calculated with the STELLA model consist of several areas which were separated by nodes. These nodes had the shape of the surface of a sphere. The table below shows the orbitals of s-, p-, d- and f-states from the left to the right and n = 1 to n = 4. The shapes also depend on the third quantum number m.
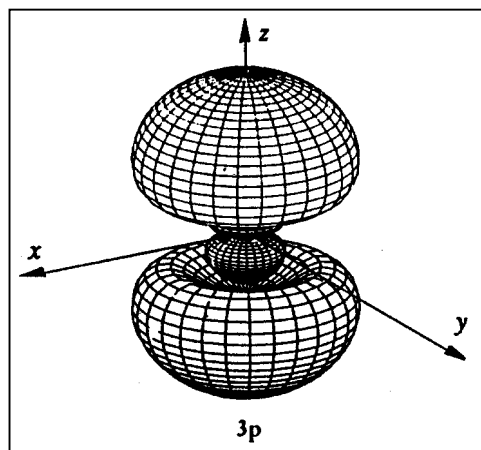
3. Higher order atoms

3.1 From the Hydrogen atom to the Helium atom

In the last chapter we discussed the Hydrogen atom in detail. Its nucleus consists of only one proton (one positive elementary charge; +1e). Therefore it can only bind one electron which forms the charge cloud around the nucleus. The state of the atom is defined by the state the electron is in; it is not necessary to distinguish between the **state of the atom** and the **state of the electron**. The potential of the Hydrogen atom is inverse proportional to the radius (V ~ 1/r).

How is a state of an atom characterized that has more than one electron (e.g. Helium)? To describe the state of a He-atom (nucleus with two positive elementary charges; +2e) we have to know the states of both electrons, because the He-nucleus can bind two electrons. Furthermore the charge clouds of the two electrons interact with each other because of the electrostatic repulsion between the negative charges. Each charge cloud is not only attracted by the positive charge of the nucleus but also repulsed by the negative charge of the other electron charge cloud. We can expect that this changes the binding energy and the distribution function compared to the Hydrogen atom. Based on these ideas, two things have to be taken into account when we go from the H-atom to the He-atom:

1. we have to change the potential V(r) because of the higher charge of the nucleus and the repulsion between the charge clouds
2. we have to calculate the binding energy and the Psi-function for both charge clouds
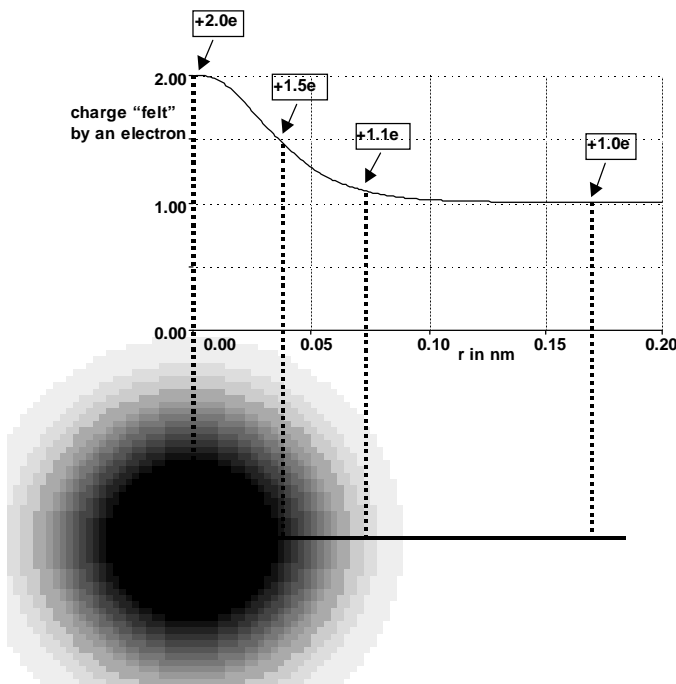
The following description gives you a first idea how the interaction between the electrons can be taken into account:

Imagine a He^{1+}-Ion (consisting of a nucleus with two positive charges and a charge cloud of one negative charge, we call the bound electron 1). The picture on the left shows this He^{1+}-Ion in the ground state. At a large distance from the nucleus (e.g. r = 0.17nm, shown in the graph) another electron (we call it electron 2) "feels" the attraction of only one positive elementary charge (+1e). The charge cloud of electron 1 with its negative charge **shields** the nucleus. When the electron 2 is coming closer to the nucleus the shielding decreases because we "dive" into the charge cloud. At a distance r = 0.07nm the electron 2 would "feel" a positive charge of 1.1e, at a distance r = 0.04nm a positive charge of 1.5e and so on. Close to the nucleus the **shielding effect** goes to zero and the full charge (double positive) of the nucleus can be "felt".

The phrase "the electron feels" should not be taken literally; it refers to the net force caused by the attraction of nucleus and the repulsion of the charge cloud. At a certain radius r only the part of the charge cloud within the radius contributes to the repulsion. The repulsion from the charge cloud outside the radius r equals out to zero. As the part of the charge cloud decreases with decreasing radius, so does the shielding.

The shielding caused by the charge cloud of electron 1 would not only affect a free electron that is approaching the nucleus (which we called electron 2) but also the second charge cloud of electron 2 in the He-atom. The potential of the first electron has to take into account the two positive charges of the nucleus and the shielding effect which depends on the distance from the nucleus. The same idea applies to the potential of the second electron.

Electron 1:
$$V_{electron1}(r) = V_{nucleus}(r) + V_{shielding}(r) = -1.44 \cdot \frac{(2 - shielding)}{r} \quad\text{.....................(16)}$$

Electron 2:
$$V_{electron2}(r) = V_{nucleus}(r) + V_{shielding}(r) = -1.44 \cdot \frac{(2 - shielding)}{r}$$

The shielding in the potential of electron 1 comes from the charge cloud of electron 2 and vice versa. We need a Schrödinger equation for each electron; the two Schrödinger equations of the He-atom are connected by the shielding.

Electron 1:
$$u''_{electron1}(r) = -26.3 \cdot (E_{electron1} - V_{electron1}(r)) \cdot u_{electron1}(r)$$

Electron 2:
$$u''_{electron2}(r) = -26.3 \cdot (E_{electron2} - V_{electron2}(r)) \cdot u_{electron2}(r)$$

The Schrödinger equations of both electrons are the same as the equation of the Hydrogen atom; only the potential has been changed. We can expect that because of the different potential we get different binding energies and u-function.

3.2 The shielding effect and potential of the Helium atom

The last section gave us a first idea how the shielding from the charge cloud affects the potential of the He-atom and thus changes the Schrödinger equation compared to the Hydrogen atom. Now, we have to find a way to calculate the shielding. It has been mentioned in the last section that at a distance r from the nucleus, only the charge within the sphere with radius r contributes to the shielding. The repulsion from the charge outside the radius r equals out to zero. Therefore when we are at a position r we just have to calculate the charge of the cloud within the radius r to get the value for the shielding. We know that Psi squared is the charge density and that Psi squared multiplied with a certain volume ΔV gives the amount of charge within the volume. So we just have to add up (integrate) Psi squared multiplied by the volume to get the charge within a radius r' which is the shielding at the radius r':

$$shielding = \int \Psi^2 \cdot dV = \int_0^{r'} \Psi^2 \cdot 4\pi \cdot r^2 \cdot dr = 4\pi \cdot \int_0^{r'} u^2 \cdot dr ....(17)$$
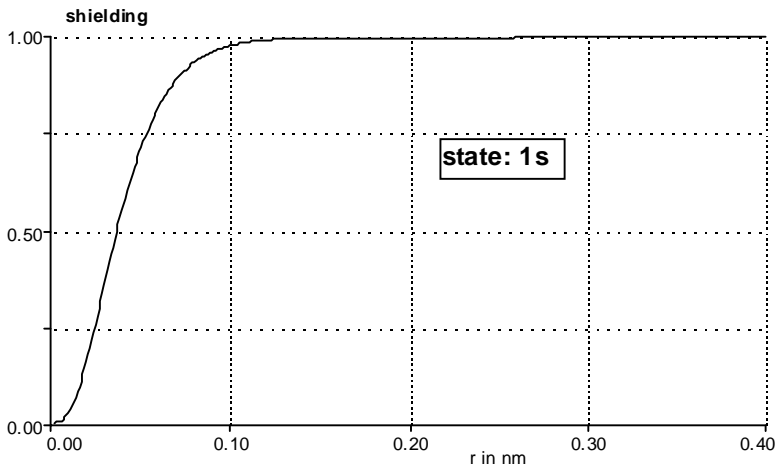
The first graph shows the shielding effect of the He^{1+}-Ion charge cloud in the ground state (1s). At the nucleus the shielding is zero. The potential contains the full charge of the nucleus. When we move away from the nucleus the shielding increases because of the increasing amount of charge within the radius r. At r = 0.04nm we find 50% of the elementary charge within the sphere with radius 0.04nm and therefore the shielding is 0.5. At this point the potential contains the equivalent of 1.5 elementary charges. The further we move away from the nucleus the smaller is the charge the potential term (–1.44/r) has to be multiplied with.
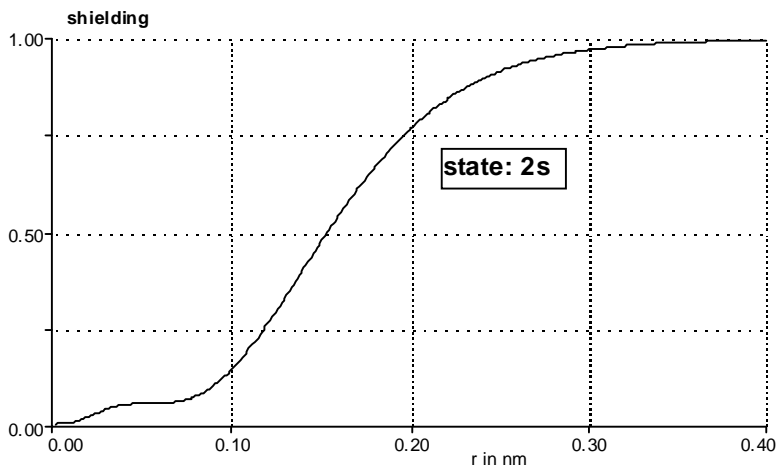
The second graph shows the shielding effect of the He^{1+}-Ion charge cloud in the first excited state (2s). Because the shielding depends on the form of the charge cloud it also depends on the state the electron is in (Psi squared changes with its state). It can be seen from the graph that the radius where the shielding is 0.5 in the 2s state is much larger (r = 0.15nm) than the radius where we find shielding = 0.5 in the 1s state (r = 0.04nm). This can be explained when we compare the charge distribution of the cloud of the 1s and the 2s state: The charge cloud of the 2s state is much larger and more spread out, the 1s charge cloud is smaller and very dense around the nucleus. Somewhere around r = 0.05nm the shielding of the 2s state does not seem to increase; it stays the same in this region. This can be explained with the node of the Psi-function that is around r = 0.05nm. At the node the charge density drops to zero. When we increase the radius around a node, the amount of charge within the radius stays nearly the same and so does the shielding.

To include the higher charge of the nucleus and the shielding in the potential V(r) we just multiply the Hydrogen potential by the **effective charge** (= charge of the nucleus minus shielding):

$$V(r) = -\frac{1.44}{r} \cdot (effective\_ch\arg e) = -\frac{1.44}{r} \cdot (2 - shielding) \quad \text{with} \quad shielding(r) = 4\pi \int_0^r u(r)^2 \cdot dr$$

In the He-atom the effective charge affecting electron 1 is the charge of the nucleus minus the shielding from electron 2 and vice versa. By calculating the potential of electron 1 with the radial distribution function of electron 2 and vice versa, we connect the two Schrödinger equations of electron 1 and 2. We can expect that whenever we change something in the Schrödinger equation of electron 1 we affect also the Schrödinger equation of electron 2

3.3 Modeling the Helium atom with STELLA

Let us try to include the ideas of the last two sections into a STELLA model. In the first section of this chapter we found that we have to:

1. change the potential V(r) because of the higher charge of the nucleus and the repulsion between the charge clouds
2. calculate the binding energy and the Psi-function for both charge clouds
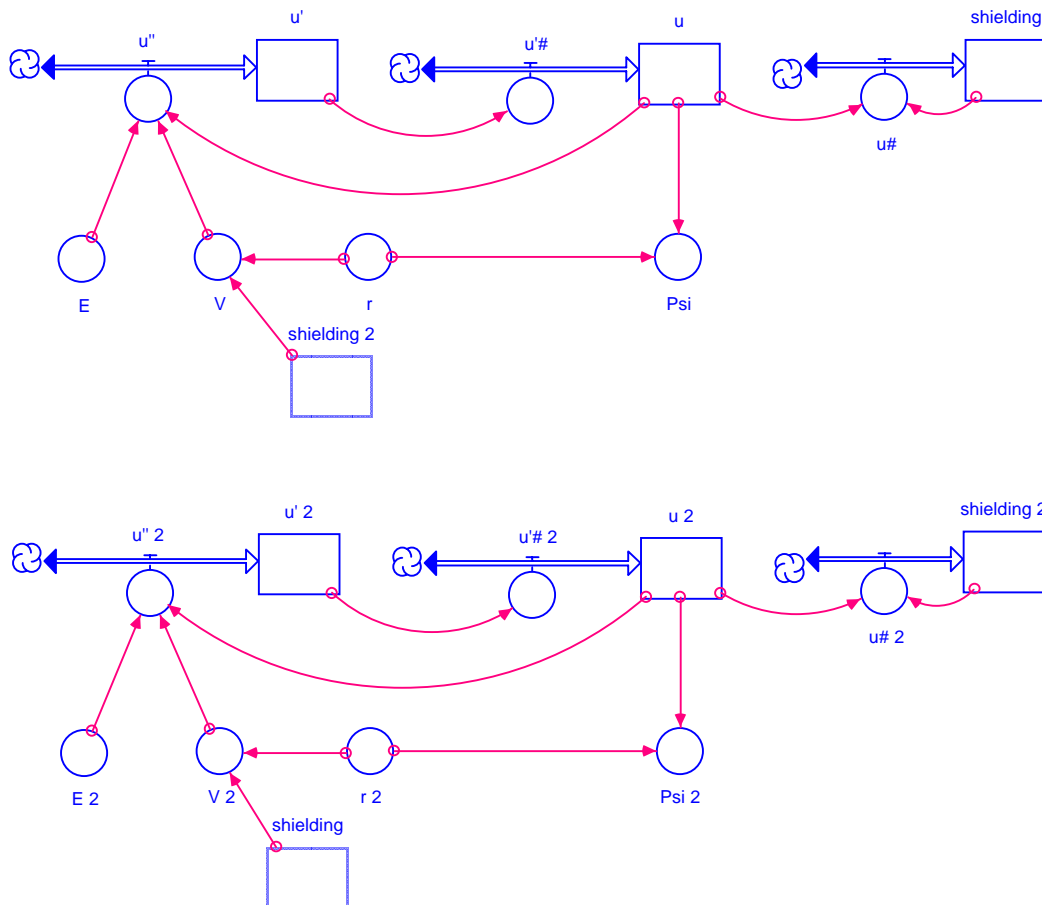
Point 2 can be done easily by copying the model of the Schrödinger equation of Hydrogen. The model above shows two Schrödinger equations (modeling the two electrons of the He-atom). Point 1 is a little more complicated: we have to model the integral over $4\pi*u(r)^2$ to calculate the shielding. This is done by the additional two objects "shielding" and "u#". "shielding" is the state variable (the result from the integration) and u# is the rate of change ($u\# = 4\pi*u(r)^2$). Because the shielding of electron 1 affects the potential of electron 2, we need a connection between these two quantities. This is done with a "STELLA-ghost" (a copy of the original object); the only purpose of ghosts is to keep the model clear. It can be seen from the model that the "ghost" of the shielding from electron one is connected to the potential of electron 2 and vice versa.

The starting value for the slope u' could have any value except zero in the model of Hydrogen. In fact the slope has to be adjusted to normalize the distribution function. We just haven't done that yet. What we mean when we talk about normalization is the following: When the charge of the cloud is integrated (or summed up) over the entire space (from zero radius to infinity), we must find one elementary charge. This also means that the shielding has to go to one asymptotically for large radii. The two shielding graphs in the previous section have been normalized by adjusting the starting value of the slope so that they reach shielding =1 asymptotically.
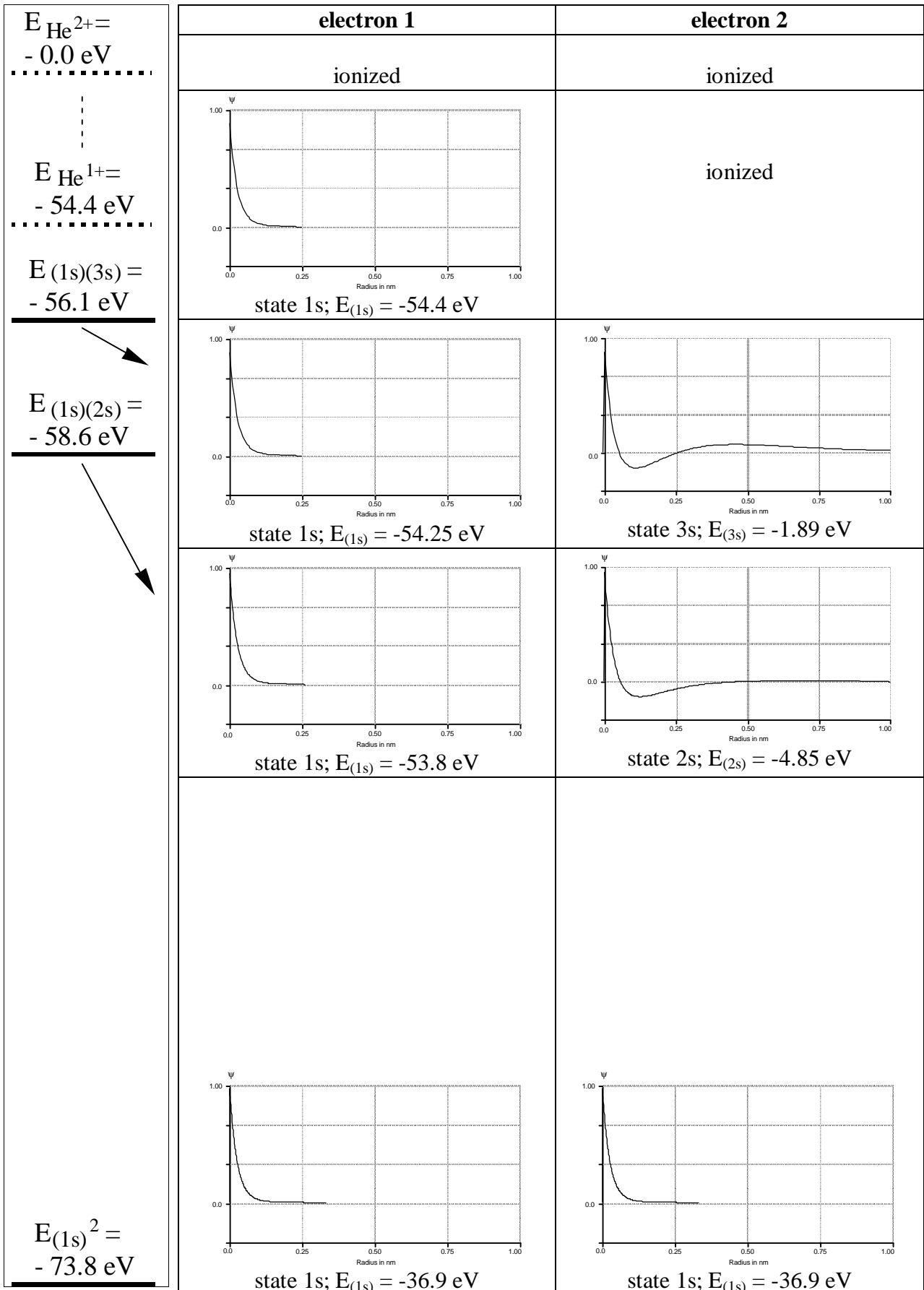
When we try to find the states of the Helium atom we have to adjust <u>four</u> quantities to fulfill <u>four</u> boundary conditions:

1. The Psi-function of electron 1 has to go to zero asymptotically
2. The Psi-function of electron 2 has to go to zero asymptotically
3. The shielding of electron 1 has to go to one asymptotically
4. The shielding of electron 2 has to go to one asymptotically

Because any change of one of these four quantities influences the Psi-functions and the shielding of both electrons, it takes much more effort to find the energy values and Psi-function for the He-atom than for the H-atom.

On the next page you find the level scheme of the Helium atom showing five selected states. The energy values and the Psi-functions have been calculated with STELLA. Because the method we have used to calculate the potential is only an approximation, the values calculated with STELLA differ a little from the measured values (see next section). The energy levels on the left are the sum of the energies of both electrons. The term "ionized" means that the electron has been completely taken away from the atom.

Level scheme of the Helium atom
(selected states calculated with STELLA)

$E_{He^{2+}} =$
$- 0.0$ eV

$E_{He^{1+}} =$
$- 54.4$ eV

$E_{(1s)(3s)} =$
$- 56.1$ eV

$E_{(1s)(2s)} =$
$- 58.6$ eV

$E_{(1s)^2} =$
$- 73.8$ eV

electron 1	electron 2
ionized	ionized
state 1s; $E_{(1s)} = -54.4$ eV	ionized
state 1s; $E_{(1s)} = -54.25$ eV	state 3s; $E_{(3s)} = -1.89$ eV
state 1s; $E_{(1s)} = -53.8$ eV	state 2s; $E_{(2s)} = -4.85$ eV
state 1s; $E_{(1s)} = -36.9$ eV	state 1s; $E_{(1s)} = -36.9$ eV

The energy scale of the level scheme has been compressed between –54.4eV and 0eV. The five selected states can be explained in the following way:

Ground state (1s)^2: At normal conditions (temperature and air pressure on earth) Helium atoms are in this state of lowest energy. Both electrons are in the 1s-state. The energy of this state is $E_{(1s)2}$ = -73.8eV.

Excited state (1s)(2s): One electron has been excited to the 2s-state (e.g. via electron collision or absorption of a photon). The energy of this state calculated with STELLA is $E_{(1s)(2s)}$ = -58.6eV. The energy difference between this state and the ground state is $\Delta E = E_{(1s)(2s)} - E_{(1s)2}$ = -58.6eV + 73.8eV = 15.2eV.

Excited state (1s)(3s): One electron has been excited to the 3s-state. The energy of this state calculated with STELLA is $E_{(1s)(3s)}$ = -56.1eV. The energy difference between this state and the ground state is $\Delta E = E_{(1s)(3s)} - E_{(1s)2}$ = -56.1eV + 73.8eV = 17.7eV. Between this state and the singly ionized Helium (He^{1+}-Ion) are infinitely many more states (like (1s)(4s), (1s)(5s), ...).

Singly ionized Helium (1s): One electron has been removed from the atom (this is called the He^{1+}-Ion). The remaining electron is in the 1s-state. . The energy of this state calculated with STELLA is $E_{(1s)}$ = -54.4eV (this is 4*(-13.6eV), the ground state energy of the Hydrogen atom). The energy difference between this state and the ground state is $\Delta E = E_{(1s)} - E_{(1s)2}$ = -54.4eV + 73.8eV = 19.4eV. The remaining electron can also be in higher states (like (2s), (3s), ...).

Doubly ionized Helium: Both electrons have been removed from the atom. The doubly ionized Helium consists only of the nucleus. The energy of this state is <u>zero by definition</u>.

In this description we have to distinguish between the **state of an electron** and the **state of the atom**. In the ground state (1s)^2 (which is an abbreviation of (1s)(1s)), both electrons are in the 1s-state. An atomic state (1s)(2s) indicates that one electron is in the 1s-state and the other in the 2s-state.

Have a look at the <u>atomic</u> states (1s)^2 and (1s)(2s). When we compare the energy of the <u>first electron</u> (in the 1s-state) we can see that it changes from E = -36.9eV to E = -53.8eV, although the electron remains in the 1s-state. This can be explained with the shielding effect. When the <u>second electron</u> is also in the 1s-state, its charge cloud is very dense around the nucleus and the shielding created by the second electron is large at small radii. When this electron is excited into a higher state (e.g. 2s), its charge cloud expands and the shielding decreases at small radii. Therefore the first electron (remaining in the 1s-state) can "feel" more of the nucleus charge and is tighter bound. This tighter binding goes along with a higher binding energy.
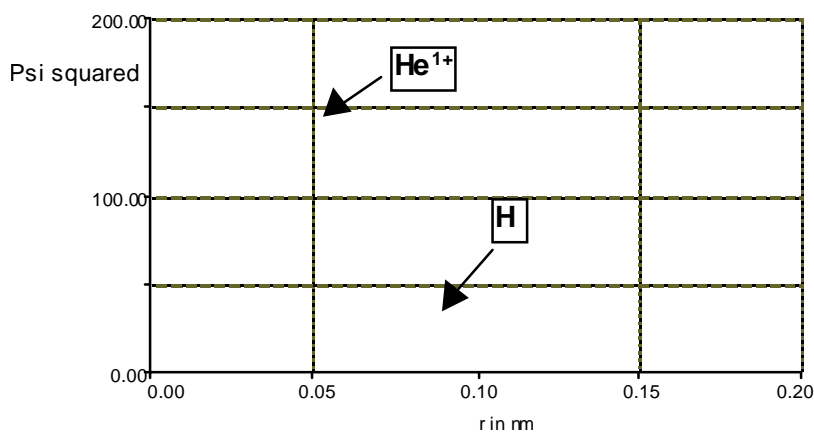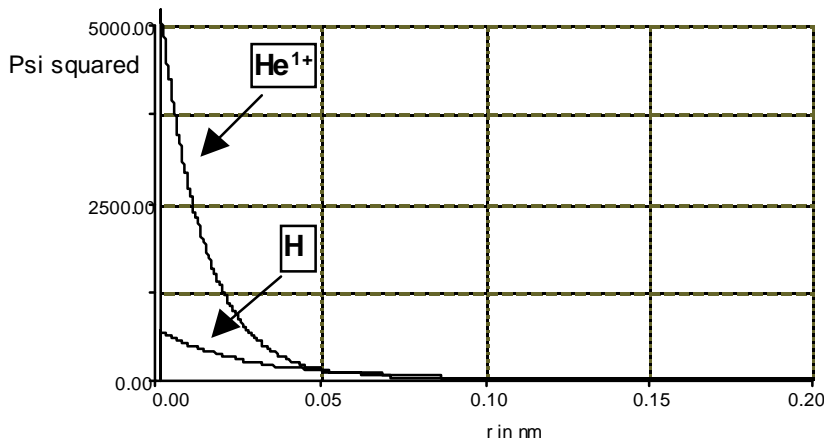

In general, a larger effective charge in the potential increases the binding energy and increases the charge density around the nucleus. This can be seen from a comparison between the H-atom (effective charge +1e) and the He^{1+}-Ion (effective charge +2e):

The first graph on the left compares the Psi squared functions of the H-atom and the He^{1+}-Ion. It can be seen that the charge density around the Helium nucleus is much larger than around the Hydrogen nucleus. The higher charge creates a deeper potential which results in a higher binding energy and a higher charge density around the nucleus.

The second graph enlarges the region of the first graph of Psi squared between 0 and 200e/nm^3 (the unit of Psi squared is charge per volume or probability per volume). The Psi squared function of the He^{1+}-Ion drops down to zero much faster than the function of the H-atom. At radii larger than roughly 0.06nm, the charge cloud of the H-atom is more dense than the charge cloud of the He^{1+}-Ion. Both Psi squared functions have been normalized.

3.4 The spectrum and size of the Helium atom
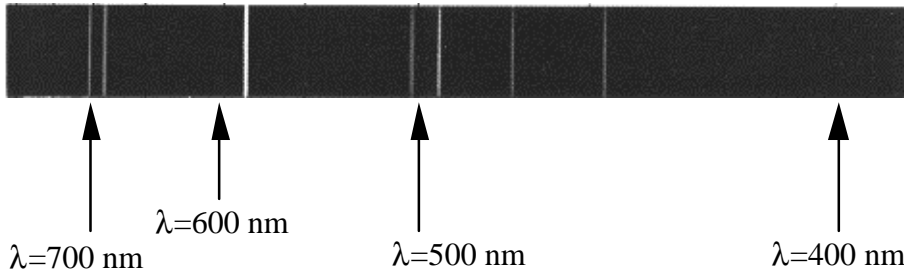
Like the Hydrogen spectrum, the <u>Helium spectrum</u> shows lines in the visible region of light (between 400nm and 800nm). Again, the most lines cannot be seen by the eye because they lie in the UV- or IR-region. On the left you can see the visible section of the He-spectrum. The scale for the wavelength is non-linear. A few lines can be seen in the region between 700nm and 450nm. The table below compares the transitions (energy differences) from measurement and STELLA calculation of a few lines.

Transition	energy difference calculated with STELLE	wavelength calculated with STELLE	measured wavelength	measures energy difference	color
$(1s)(2s) \rightarrow (1s)^2$	15.2 eV	81.6 nm	58.4 nm	21.2 eV	UV
$(1s)(3s) \rightarrow (1s)^2$	17.7 eV	70.0 nm	53.7 nm	23.1 eV	UV
$(1s)(3s) \rightarrow (1s)(2s)$	2.5 eV	496 nm	668 nm	1.9 eV	red
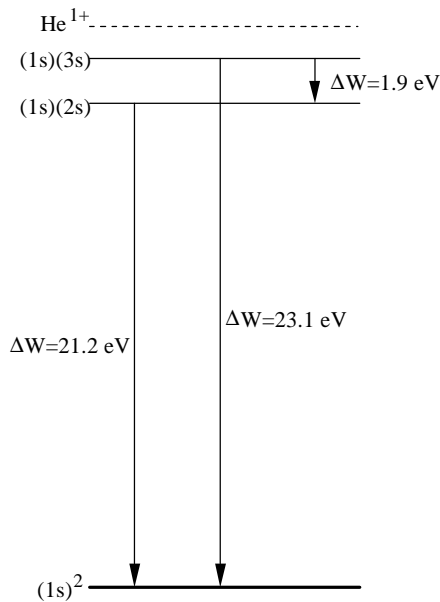
The picture on the left shows the energy levels and the transitions between the three states $(1s)^2$, $(1s)(2s)$ and $(1s)(3s)$ with the <u>measured</u> energies. When the atom goes from the state $(1s)(3s)$ to $(1s)(2s)$ it emits visible light of the energy $\Delta E = 1.9eV$. This corresponds to a wavelength of $\lambda = 668nm$. The red line can be seen in the line spectrum. The two other transitions correspond to lines in the UV- region. The other visible lines correspond to transitions between higher states.

The states calculated with STELLA differ from the experimental values up to 30%. This shows us that the approximation of the potential with the shielding does not give exact values but gives a good idea of the region where the energy of a state can be found. The reason why the shielding is just an approximation comes partly from the fact, that the calculation of the potential at radius r takes into account the charge inside the sphere with radius r but not the charge outside and that transitions occur e.g. from p-states to s-states (and not among s-states).

Because the Psi squared functions are not so sensitive against changes in the energy value, the functions differ not much from the precisely calculated functions.
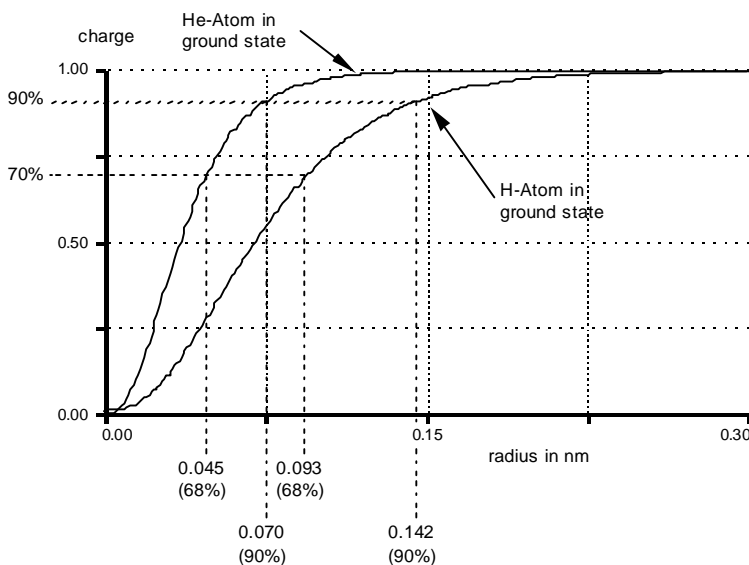

From both definitions of the radius r (70% or 90% of the charge inside a sphere of radius r) can be seen that the He-atom in its ground state is only half the size of the H-atom. This result is qualitatively in agreement with measurements of the van der Waals radius (see table in section 2.7), although the measurement only shows a difference of about 20%.

Although the Helium atom has two electrons, the Helium atom is smaller than the Hydrogen atom.

3.5 Atoms above Helium

In this last section we want to generalize the results from the Hydrogen and the Helium atom to get an idea how the states of <u>any</u> atom can be calculated with the Schrödinger equation and to explain the periodic table of elements. The elements above Helium differ in the amount of positive charges and the number of bound electron (e.g. Lithium 3, Beryllium 4, Boron 5, ...). The third electron in Lithium cannot be in the 1s-state but has to be in the 2s-state. This is a result from the elementary behavior of electrons: <u>every state can only be occupied by one electron</u>. This is called the **Pauli exclusion principle**. The two electrons in the 1s-states in Helium differ by the spin quantum number (see Serway section 42.3) and are therefore not in the same state (but both are in a state with quantum number 1s). The third electron in Lithium has to be in the 2s-state because of the Pauli principle. Because the charge cloud of this electron is more spread out than the charge clouds of the electrons in the 1s-state, the shielding effect for the third electron is greatest. The low binding energy of the third electron is not only a result of the higher state (2s) but also because the effective charge in the potential for the third electron is close to one because of the shielding of the two other electrons.
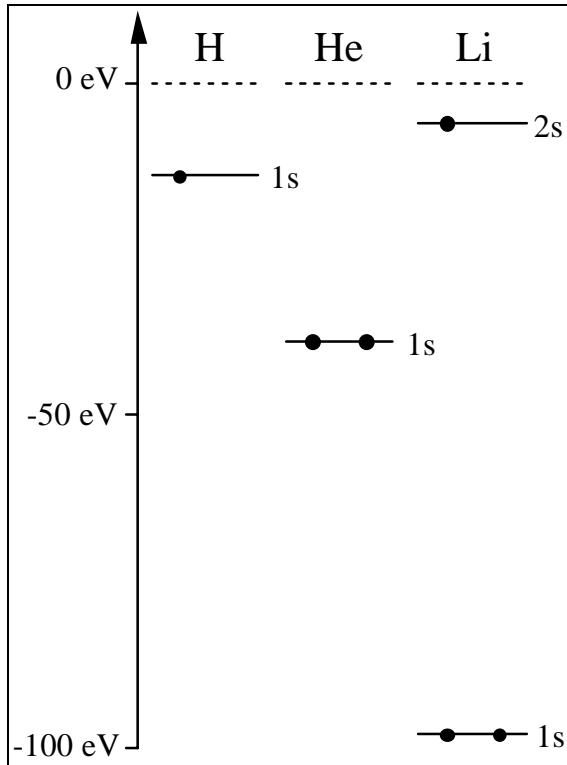
The following values show how the shielding effects the energy: The energy of only one electron around the <u>Lithium^{2+}-Ion</u> in the 2s-states is E = -30.7eV. Because of the shielding from the two other electrons, the energy of the third electron in the 2s-state in the <u>Lithium-atom</u> is E = -5.8eV (much less bound).

The picture on the left compares the ground state energy levels of Hydrogen, Helium and Lithium. The binding energy of the 1s-state increases with the nucleus charge. This leads to larger charge densities around the nucleus of charge clouds in the 1s-state. This was the reason why the He-atom was smaller than the H-atom. But because the third electron in the Lithium atom has to be in the 2s-state, the Li-atom is much larger than the He-atom, as can be seen in the table on page 17.
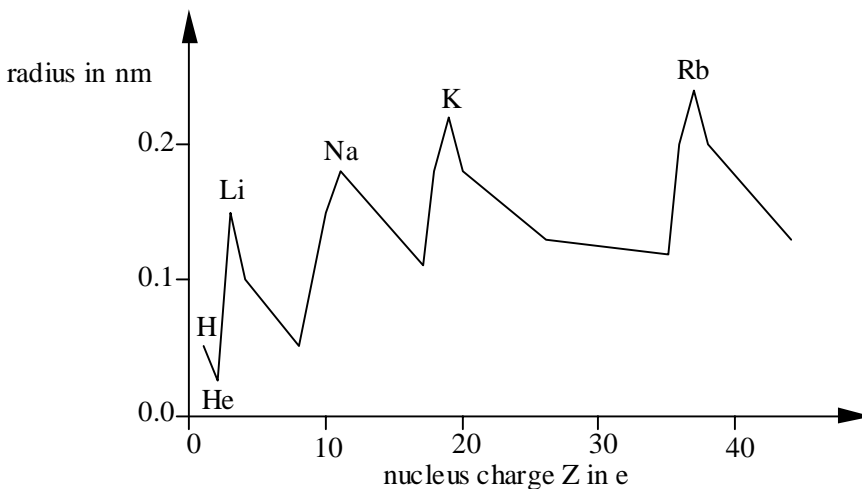
The table on the left shows the radius of the first 40 elements from the periodic table. Between Lithium and Sodium, the radius decreases with increasing nucleus charge, but at Sodium the radius increases drastically. The last electron in Sodium occupies a higher state and therefore Sodium has a much larger radius.