

### Models of the atom

Based on the results of experiments that showed that atoms contain electrons, combined with the fact that atoms are neutral, lead to the conclusion that the atom must also contain positive charges. Although the dimensions of the atom were known, it was not clear how the charges were distributed. **Thomson** developed a model of the atom in which the atom was assumed a sphere of positive charge with electrons embedded. The **Thomson model** has the following features:

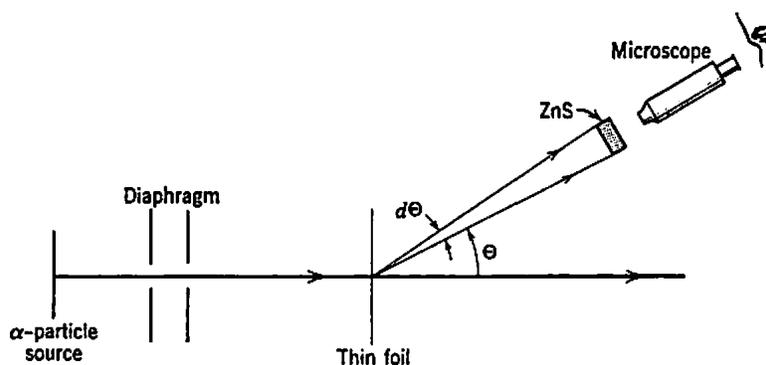
1. In the ground state, the electrons are fixed at their equilibrium positions.
2. In excited states, the electrons are vibrating around their equilibrium positions.

But ..... vibrating electrons will produce EM waves. Although this was qualitatively in agreement with the observation the atoms in excited states emit radiation, quantitatively the predictions of this model did not agree with the observed EM waves.

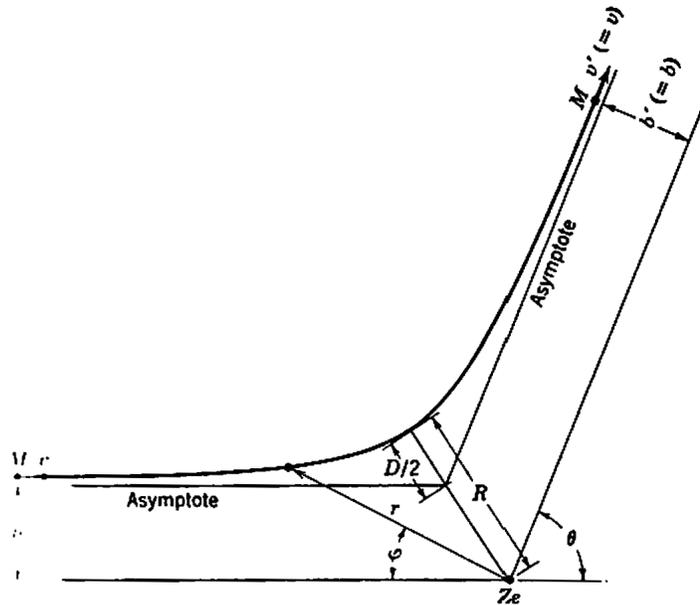
The experiments by **Rutherford**, who studied the scattering of  $\alpha$  particles from atoms (see Figure below), showed convincingly that the Thomson model of the atom was not correct. Rutherford observed large deflections of  $\alpha$  particles with finite probability. Consider the following facts:

1. Since  $m_e \ll m_\alpha$ , the deflection due to scattering of electrons is small. Large deflections thus require a large number of small-angle scatterings. If we rely on multiple scattering to produce backward deflection (scattering by angles between  $90^\circ$  and  $180^\circ$ ) the fraction of  $\alpha$  particles that would be observed at angles beyond  $90^\circ$  is  $10^{-3500}$ . The observed fraction is  $10^{-4}$ , much larger than the expected fraction based on multiple scattering.
2. Large deflections require strong Coulomb repulsion that cannot be provided if the positive charge is distributed evenly over the volume of the atom. If we require that the  $\alpha$  particles are backscattered due to a single interaction, the positive charge must be located in a volume with a diameter of  $10^{-14}$  m.

Rutherford developed a theory to describe the observed scattering distributions. His theory has the following features:



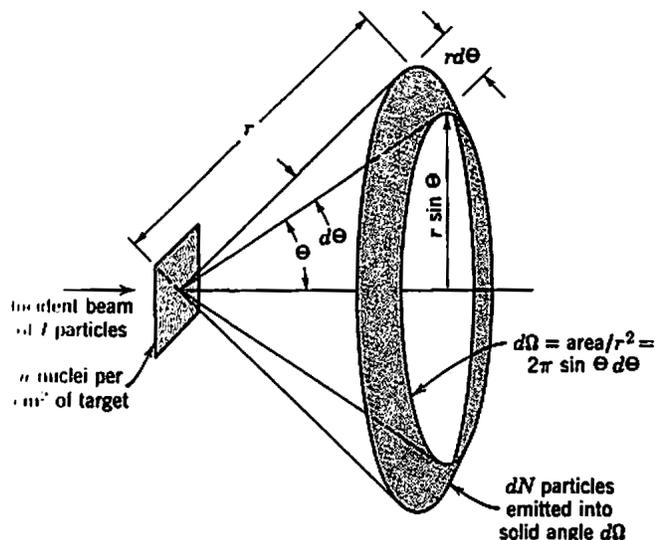
1. Each incident  $\alpha$  particle has a well-defined impact parameter  $b$ .
2. There is a one-to-one correlation between the impact parameter and (a) the scattering angle  $\theta$  and (b) the distance of closest approach  $R$ .
3. The smallest value of  $R$  occurs when there is a head-on collision ( $b = 0$ ).



In the Rutherford experiment, the detector used to detect the scattered  $\alpha$

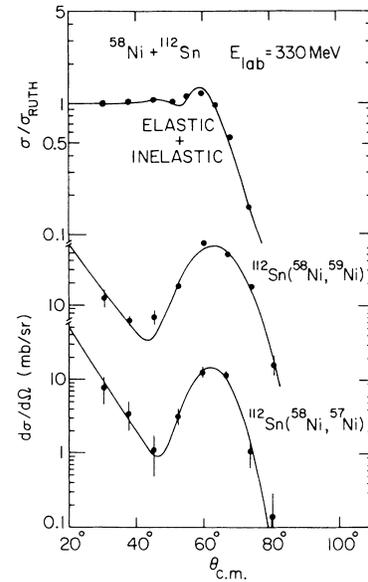
particles has a well-defined cross sectional area (effective detection area). Consider for a moment that the scattered  $\alpha$  particles are distributed uniformly in all directions. In this case, the rate of detection will be the same at all positions of the detector. However, if we want to plot the rate as function of the polar angle  $\theta$  we need to take into consideration that the number of scattered particle scattered by  $90^\circ$  is going to be much larger than the number of particles scattered by  $0^\circ$  or  $180^\circ$ . This is a direct consequence of the phase space available for scattering. When the detector is positioned at a certain scattering angle  $\theta$  the fraction of all particles scattered with a scattering angle between  $\theta$  and  $\theta + d\theta$  depends on the angle. As a result, if we want to look at the scattering rate as function of the polar angle  $\theta$ , the “trivial” angle dependence should be removed if we want to focus on the underlying physics. As can be seen in the Figure at the bottom right of this page, the number of particles scattered with an angle between  $\theta$  and  $\theta + d\theta$  is proportional to  $2\pi \sin\theta d\theta$ . The measured scattering rates as function of angle are corrected for this “phase-space” dependence of the detector response. The remaining angular dependence will reflect the underlying physics.

After applying the solid-angle correction, Rutherford obtained the following equation for the scattering rate:



$$\frac{d\sigma}{d\omega} = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \left(\frac{Z_\alpha Z_{\text{target}}}{E_\alpha}\right)^2 \frac{1}{\sin^4\left(\frac{\theta}{2}\right)}$$

This expression described the observed angular distributions remarkably well, confirming Rutherford’s model of the atom. When the energy of the  $\alpha$  particles increases, the distance of closest approach decreases and at one point the  $\alpha$  particles may start to feel the influence of the strong nuclear force. At this point, differences from Rutherford scattering are observed and the energy and angle at which this occurs can be used to determine the size of the nucleus. This technique is still being used to study nuclear size. For example, in the Figure on the right, the results of study of collisions between Ni nuclei and Sn nuclei are shown. The rate of elastic scattering divided by the rate of Rutherford scattering shows that at about  $60^\circ$  the influence of the nuclear force becomes important. Knowing the nuclei involved and their energies, we can determine the distance between the centers of the nuclei when they “touch” – note: the nuclear force has a short range and requires the nuclear surfaces to almost touch before it becomes a factor in the dynamics of the interaction.



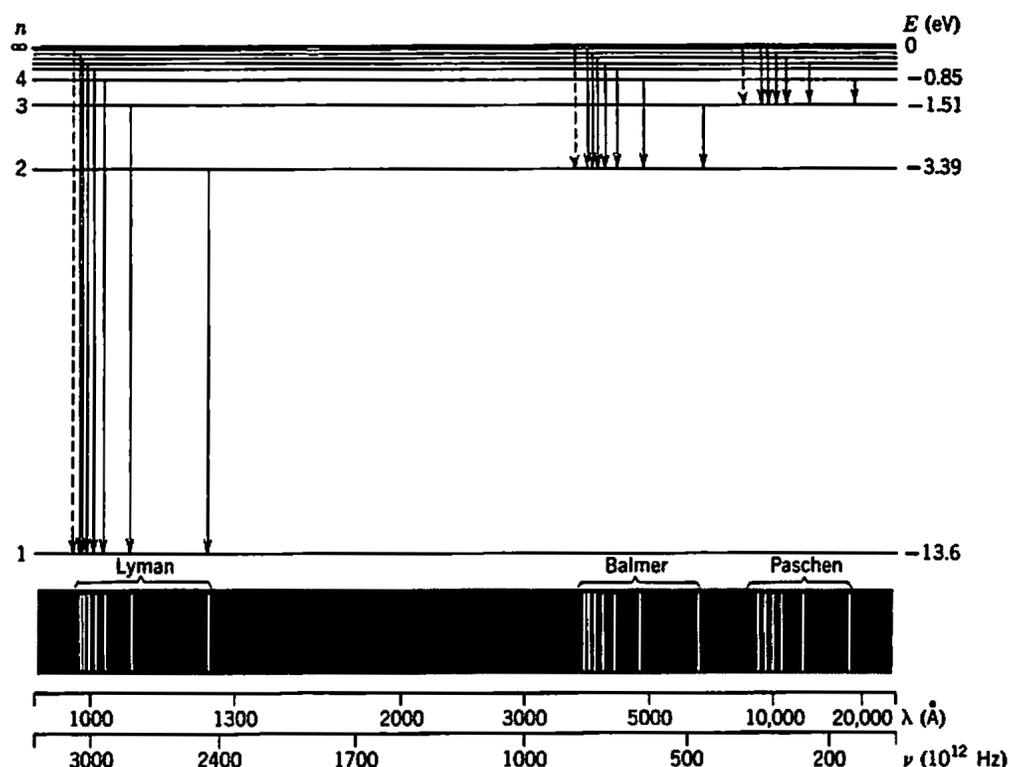
### Atomic Spectra

Studies of the emission spectra of atoms have shown that the light they emit is composed of light with discrete wavelengths. The simplest atom to study is the Hydrogen atom, which has one proton as its nucleus and one electron. The Hydrogen spectrum is found to be very simple. Measurements of the wavelengths revealed that the light emitted can be grouped in various series. One of these series is the **Balmer series**. The wavelengths of the light in this series can be described by the following equation:

$$\lambda = 3646 \frac{n^2}{n^2 - 4}$$

or

$$\kappa = \frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$$



where  $R_H$  is the **Rydberg constant** for Hydrogen. These relations are empirical formulas that were derived on the basis of the observed wavelengths. Similar relations were found for other series, such as the Lyman and Paschen series.

**Niels Bohr** was the first person to explain the observations that were made. He developed a model, called the **Bohr model**, which predicted the levels in Hydrogen. Based on the predicted level scheme, predictions can be made about the wavelengths that are present in the emission spectrum of Hydrogen. Bohr showed that the Balmer series was due to transitions to the first excited state in Hydrogen. The Lyman and Paschen series were due to transitions to the ground state and the second excited states, respectively. In 1922, Bohr received the Nobel Prize in Physics for his development of the Bohr model.

Bohr made the following assumptions when he developed his model:

1. The electrons move in circular orbits.
2. The angular momentum of the electron is quantized:  $L = n\hbar$  where  $n = 1, 2, 3, \dots$
3. The orbits are stable; no radiation is emitted, even though the electrons accelerate.
4. Radiation is emitted when transitions occur between different energy levels.

Note: these assumptions are a mixture of classical and non-classical physics.

In order for the electrons to move in circular orbits, we must require that

$$\frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e(Ze)}{r^2}$$

The quantization of the angular momentum requires that

$$mvr = n\hbar$$

These two equations allow us to determine both  $v$  and  $r$  for a given value of  $n$ . Based on this information, the total energy of the electron can be determined:

$$E_n = \frac{1}{2}m_e v^2 - \frac{1}{4\pi\epsilon_0} \frac{e(Ze)}{r} = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{m_e e^2 (Ze)^2}{(2\hbar^2)} \frac{1}{n^2} \quad n = 1, 2, 3, \dots$$

Note that the total energy of the electron is negative. When the energy is positive, the electron is unbound.

The predictions made with this model agree very well with experimental values. The model predicted lines that had not been observed at that time; these lines were confirmed to later.

Precise measurements showed that corrections must be made for the nuclear mass. Instead of using the mass of electron,  $m_e$ , the reduced mass  $\mu$  should be used:

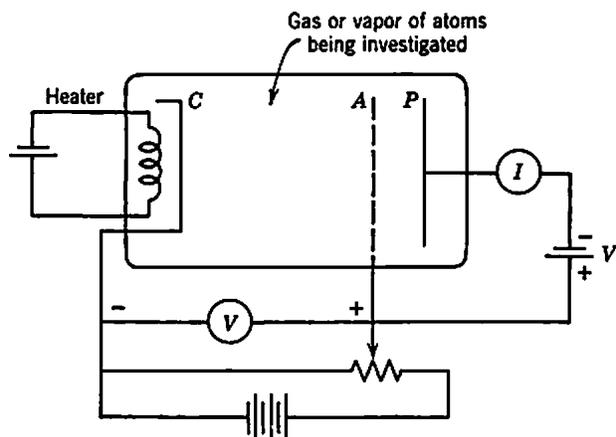
$$\mu = \frac{m_e M_{nuc}}{m_e + M_{nuc}}$$

As a result of this change, the Rydberg constant for Hydrogen changes by 1 part in 2000. After making this correction, it was observed that the predicted wavelengths of the emission lines agree to within 3 parts of 100,000 with the observed wavelengths.

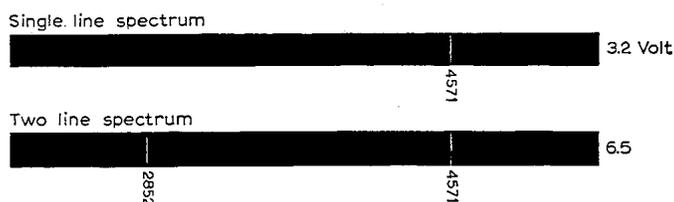
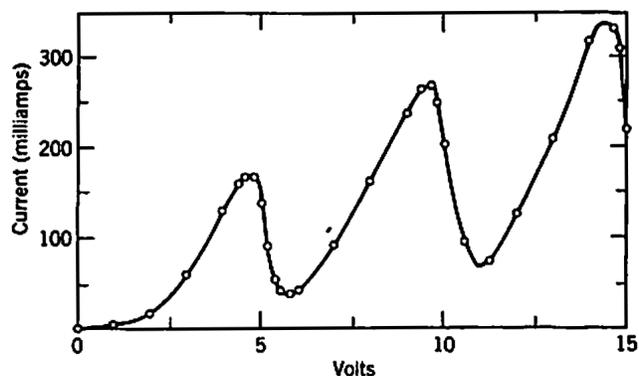
The quantization of the energy states of atoms was confirmed directly with a simple experiment performed by **Frank and Hertz** in 1914. In 1925 they received the Nobel Prize in Physics for their work.

The Frank and Hertz experiment is schematically shown in the Figure at the bottom of the page. Key aspects of the experiment are:

1. The electrons are accelerated by a potential difference  $V$  between the cathode (C) and the anode (A).



2. The maximum kinetic energy of the electrons upon reaching  $A$  is  $eV$ .
3. A retarding potential exist between  $A$  and  $P$ . Electrons that pass  $A$  must have a minimum kinetic energy ( $eV_r$ ) to reach  $P$ .
4. The current collected at  $P$  is measured as function of the accelerating potential  $V$ . The current is directly proportional to total charge collected at  $P$ , and thus to the number of electrons reaching  $P$ .
5. The measured current show significant dips at 4.9 V, 9.8 V, etc.
6. When the potential is 4.9 V, the electrons have an energy of 4.9 eV upon reaching the anode  $A$ . The dip indicates that a significant number of electrons are removed from the current; they must have lost most of their energy so that they now have an energy that is too low to reach  $P$ . The first excited state in Hg must be located around 4.9 eV.
7. The dip at 9.8 V corresponds to the loss of electrons that have two interactions, loosing 4.9 eV at each interaction.
8. As the maximum energy of the electrons increases, excitation of higher-lying states becomes possible. Once the atoms are excited, they will decay back to their ground state via the emission of photons. These photons can be detected. The two spectra shown below show the emission spectrum obtained from an experiment with Mg vapor at two different acceleration voltages. At 3.2 V, only one state in Mg can be excited; at 6.5 V two states can be excited (remember: a shorter wavelength corresponds to a larger energy).



### Quantization postulates

The assumption made by Bohr that the angular momentum of the electron is quantized is a special case of the **Wilson-Sommerfeld quantization rules**. The quantization rules apply to any system with a coordinate  $q$  that is a periodic function. **Note:** a periodic function requires that the time dependence of a coordinate  $q$  repeats itself after well-defined periods of time (the period) but the time dependence of  $q$  does not have to be harmonic. For this type of motion, the

Wilson-Sommerfeld quantization rule states that the linear momentum  $p_q$  associated with coordinate  $q$  must satisfy the following condition:

$$\oint_{\text{One period}} p_q dq = n_q h$$

where  $n_q$  is the quantum number (an integer).

**Example 1**

Consider one-dimensional, non-relativistic, simple-harmonic motion. The total energy associated with this motion is equal to

$$E = \frac{p_x^2}{2m} + \frac{1}{2} kx^2$$

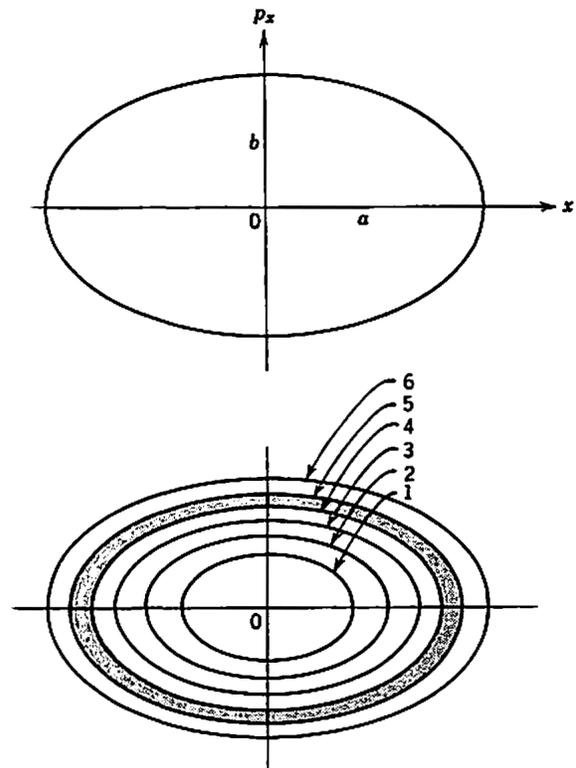
This equation can be rewritten in the following way:

$$\frac{p_x^2}{2mE} + \frac{x^2}{2E/k} = 1$$

and describes an ellipse in  $p_x$  versus  $x$  space. The state of the system at  $t = 0$  is represented by a point on this ellipse. As time evolves, this point follows the path described by the ellipse and after one period will return to its starting point. In order to apply the Wilson-Sommerfeld quantization rule we need to evaluate the integral of  $p_x$  during one period. This is equal to the area of the ellipse:

$$\oint_{\text{One period}} p_x dx = \pi \sqrt{\frac{2E}{k}} \sqrt{2mE} = \frac{2\pi E}{\sqrt{k/m}}$$

Since the motion is simple-harmonic motion,  $\sqrt{k/m}$  is equal to  $\omega$  or  $2\pi\nu$  where  $\nu$  is the frequency of the oscillation. The quantization rule can now be rewritten as



$$\frac{2\pi E}{2\pi\nu} = \frac{E}{\nu} = nh$$

or

$$E = nh\nu$$

which is Planck's quantization rule.

### Example 2

Consider an object carrying out rotational motion with a constant angular momentum  $L$ . In this example, the position coordinate is the angle  $\theta$  and the associated momentum is  $L$ . Applying the Wilson-Sommerfeld quantization rule results in the following relation:

$$\oint_{\text{One period}} L d\theta = L \oint_{\text{One period}} d\theta = 2\pi L = nh \Rightarrow L = n \frac{h}{2\pi} = n\hbar$$

which is Bohr's quantization rule.

The Wilson-Sommerfeld quantization rule can also explain the **hyperfine splitting** in the Hydrogen spectrum. Consider an electron in an elliptical orbit around a proton. The orbit can be described in terms of two position coordinates: the radius  $r$  and the polar angle  $\theta$ . The two momenta associated with these position coordinates are the linear momentum  $p_r$  and the angular momentum  $L$ . The Wilson-Sommerfeld quantization rule requires that

$$\oint L d\theta = n_\theta h$$

$$\oint p_r dr = n_r h$$

Since angular momentum is conserved, assuming we consider the electrons and the proton as our system, we can rewrite the first quantization requirement as

$$\oint L d\theta = L \oint d\theta = 2\pi L = n_\theta h \Rightarrow L = \frac{n_\theta h}{2\pi} = n_\theta \hbar \quad \text{where } n_\theta = 1, 2, 3, 4, 5, \dots$$

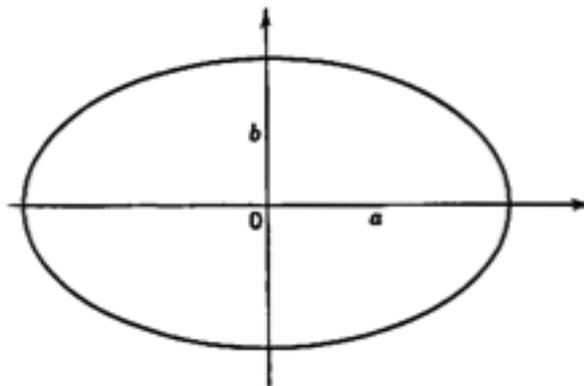
Note that this quantization condition is the same as the condition we obtained for a circular orbit. For a circular orbit, the radial component of the linear momentum,  $p_r$ , is equal to 0 and the quantum number  $n_r$  must thus be 0. Values of  $n_r$  different from 0 correspond to elliptical orbits

with a semi-major axis equal to  $a$  and a semi-minor axis equal to  $b$ . For such an orbit we can evaluate the integral of  $p_r$  and find that it is equal to

$$\oint p_r dr = 2\pi L \left( \frac{a}{b} - 1 \right) = n_r h$$

The eccentricity  $\varepsilon$  of the elliptical orbit is defined as

$$\varepsilon = \sqrt{1 - \left( \frac{b}{a} \right)^2}$$



A circular orbit has an eccentricity of 0. The product of the eccentricity  $\varepsilon$  and the distance  $a$  is the distance between the center of the ellipse and one of the focal points where the proton is located.

At the positions where  $r = a(1 \pm \varepsilon)$  the radial component of the linear momentum of the electron will be zero. At these positions, the total energy of the electron will be the sum of the potential energy and rotational kinetic energy (which can be expressed in terms of the angular momentum of the electron):

$$E = U(r) + \frac{1}{2} \frac{L^2}{\mu r^2} = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} + \frac{1}{2} \frac{L^2}{\mu r^2}$$

The angular momentum  $L$  can be expressed in either quantum number  $n_r$  or  $n_\theta$ :

$$L = n_\theta \hbar = \frac{n_r \hbar}{\frac{a}{b} - 1}$$

The two quantum numbers are thus connected to each other:

$$n_\theta \left( \frac{a}{b} - 1 \right) = n_r$$

This equation can be rewritten as a relation between  $b$  and  $a$ :

$$n_\theta (a - b) = n_r b \Rightarrow a n_\theta = b(n_r + n_\theta) = b n \Rightarrow b = a \frac{n_\theta}{n}$$

The integer  $n$  is called the **principal quantum number**; the integer  $n_\theta$  is called the **azimuthal quantum number**. The semi-major axis  $a$  can be calculated by applying the condition for mechanical stability of elliptical orbits (see Physics 235):

$$a = \frac{4\pi\epsilon_0}{Ze^2} \frac{n^2\hbar^2}{\mu}$$

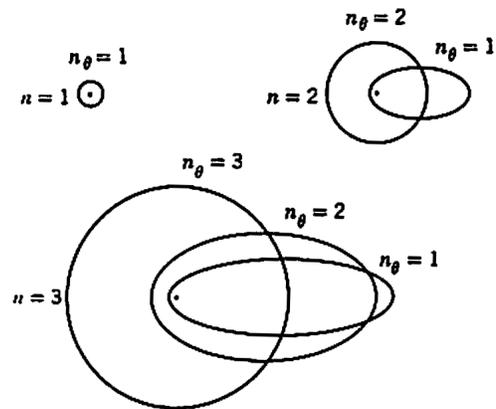
Although we do not have to the time to derive this relation, we can quickly check that it is consistent with a circular orbit for which stability requires that

$$F_{electric} = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{a^2} = \frac{\mu v^2}{a} = \frac{1}{a} \frac{a^2 \mu^2 v^2}{\mu a^2} = \frac{L^2}{\mu a^3} \Rightarrow a = \frac{4\pi\epsilon_0}{Ze^2} \frac{L^2}{\mu} = \frac{4\pi\epsilon_0}{Ze^2} \frac{n_\theta^2 \hbar^2}{\mu} = \frac{4\pi\epsilon_0}{Ze^2} \frac{n^2 \hbar^2}{\mu}$$

The total energy of the system is found to be equal to

$$E = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{\mu(Ze^2)^2}{2n^2\hbar^2}$$

Typical orbits of the electron for three values of  $n$  are shown in the Figure. According to the equation for  $E$ , electrons in the two orbits for  $n = 2$  have the same energy. These orbits are said to be **degenerate**. Experiments show that different orbits for the same value of  $n$  have slightly different energies. To explain these energy differences we must treat the orbits using relativistic mechanics; this leads to the following expression for the energy:



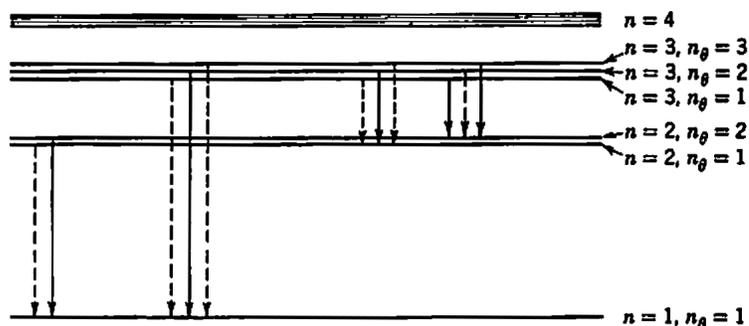
$$E = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{\mu(Ze^2)^2}{2n^2\hbar^2} \left\{ 1 + \frac{\alpha^2 Z^2}{n} \left[ \frac{1}{n_\theta} - \frac{3}{4n} \right] \right\}$$

In this equation,  $\alpha$  is the **fine structure constant** which is approximately equal to  $1/137$ . As we can see, orbits with the same  $n$  but different  $n_\theta$  have different energies and the degeneracy has been removed.

The splitting is small. Consider for example the  $n = 2$  orbit. The difference between the two possible orbits is equal to

$$\begin{aligned}\Delta E &= -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{\mu(Ze^2)^2}{2n^2\hbar^2} \left\{ \frac{\alpha^2}{2} \left[ \left\{ \frac{1}{2} - \frac{3}{8} \right\} - \left\{ \frac{1}{1} - \frac{3}{8} \right\} \right] \right\} = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{\mu(Ze^2)^2}{2n^2\hbar^2} \left\{ \frac{\alpha^2}{4} \right\} = \\ &= \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{\mu(Ze^2)^2}{2n^2\hbar^2} \{1 \times 10^{-5}\}\end{aligned}$$

A few of the energy levels calculated using the relativistic expression for  $E$  are shown in the energy level diagram shown on the right. The measured wavelengths for the Hydrogen atom are in excellent agreement with predictions made using the relativistic expression for  $E$ .



The dashed arrows in the Figure show transitions that are in principle possible but are not observed. Based on the quantum numbers of the states involved in transitions, we conclude that transitions only occur when

$$n_{\theta i} - n_{\theta f} = \pm 1$$

This is an example of a **selection rule** that limits the number of possible transitions. We will encounter more of these later in this course.

### Final remarks

All results we have discussed to date have shaped the development of modern quantum mechanics. The theory of quantum mechanics must satisfy the following requirements:

1. When the quantum numbers used to describe quantum mechanical states become very large, the predictions made on the basis of the quantum theory must approach the predictions of classical physics.
2. The selection rules have to be satisfied over the entire range of quantum numbers. Selection rules obtained in the classical limit must also hold in the quantum limits and vice versa.