AKADEMIA GÓRNICZO-HUTNICZA
IM. STANISŁAWA STASZICA W KRAKOWIE

Modern physics

5. Models of simple atoms

Outline

5.1. Energy levels in the 2D and 3D infinite potential well

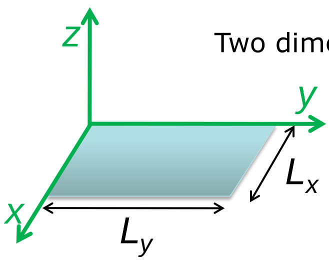
5.2. Early models of atoms

5.3. The Bohr model

5.4. Atomic spectra

5.1. Energy levels in the 2D infinite potential well

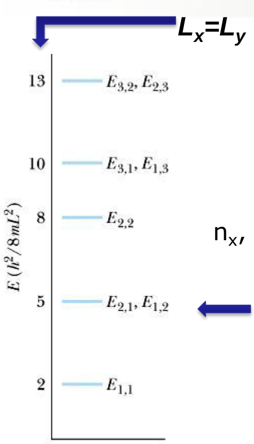
Rectangular corral
Two dimensional 2D infinitive potential well



An electron can be trapped in the rectangular area with widths L_x and L_y as in 2D infinitive potential well.
The rectangular coral might be on the surface of a body that somehow prevents the electron from moving parallel to the *z* axis and thus from leaving the surface.

Solution of Schrödinger's equation for the rectangular corral, shows that, for the electron to be trapped, its matter wave must fit into each of the two widths separately, just as the matter wave of a trapped electron must fit into a 1D infinitive potential well. This means the wave is separately quantized in L_x and L_y.

5.1. Energy levels in the 2D infinite potential well



The energy level diagram for an electron trapped in a square corral $L_x=L_y$

The energy of the electron depends on both quantum numbers and is the sum of the energy of the electron along x axis and y axis.

$$E_{nx,ny} = \left(\frac{h^2}{8mL_x^2}\right)n_x^2 + \left(\frac{h^2}{8mL_y^2}\right)n_y^2$$

n_x, n_y – quantum numbers, positive integers only

Different states with the same energy are called **degenerate**

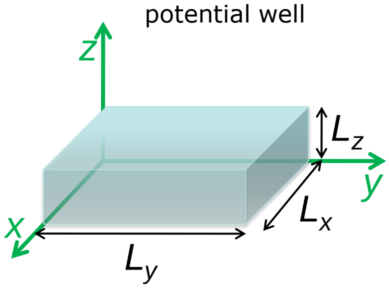
Example of degenerate states:

for $L_x=L_y$ the states characterized by quantum numbers $n_x=2$; $n_y=1$ and $n_x=1$; $n_y=2$ have the same energy $E_{21}=E_{12}$

Degenerate states cannot occur in a one-dimensional well.

5.1. Energy levels in the 2D infinite potential well

Rectangular box
Three dimensional infinitive potential well

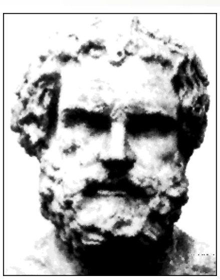


An electron can be trapped in 3 D infinitive potential well – a rectangular box with widths L_x,L_y,L_z.
Then from the Schrödinger's equation we get the energy of electron as:

$$E_{nx,ny,nz} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

In the three dimensional world (real world) there are three quantum numbers to characterize the energetic state of an electron. In the simple model of the infinite potential well (rectangular box) they are denoted as: n_x, n_y, n_z. The real 3D potential of an atom is more complicated but still we get three quantum numbers.

5.2. Early models of atoms



Democritus(400 BC)

The Greek philosopher Democritus began the search for a description of matter more than 2400 years ago.
He asked: Could matter be divided into smaller and smaller pieces forever, or is there a limit to the number of times a piece of matter could be divided?

He named the smallest piece of matter "atomos", meaning "not to be cut."

5.2. Early models of atoms

Thomson's Plum Pudding Model

J.J. Thomson(1856-1940)

In 1897, the English scientist J.J.Thomson provided the first hint that an atom is made of even smaller particles.

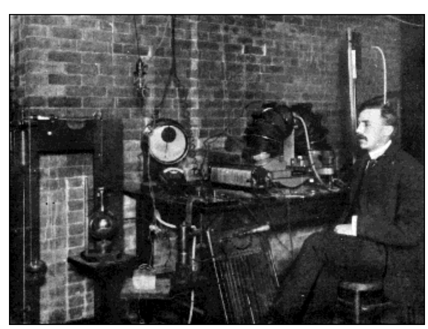
He proposed a model of the atom that is sometimes called the "**plum pudding**" model.

In this historical model, atoms are made from a positively charged substance with negatively charged electrons embedded at random, like raisins in a pudding.

5.2. Early models of atoms

Rutherford's Gold Foil Experiment

In 1908, the English physicist Ernest Rutherford carried out a scattering experiment that revealed the atomic structure.



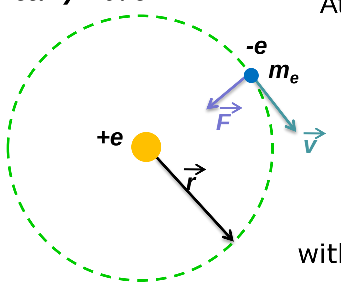
Ernest Rutherford (1871-1937)

According to Rutherford all of an atom's positively charged particles are contained in the nucleus while the negatively charged particles can be found dispersed outside the nucleus.

5.2. Early models of atoms

Planetary model of the hydrogen atom

Planetary Model



Atom (neutral) = nucleus (+*e*) + electrons (-*e*)

The electron moves on circular orbits around the nucleus under the influence of the Coulomb attraction force

$$F = k\frac{|q_1||q_2|}{r^2}$$

with $k = \frac{1}{4\pi\varepsilon_0}$

q_1 is a charge −e of the electron

q_2 is a charge +e of the nucleus

Coulomb force acts on electron producing a centripetal acceleration

$$a = \frac{v}{r^2}$$ v - is the electron velocity

5.2. Early models of atoms

Orbit radius can be calculated classically from the **Newton's law**

We can write Newton's second law for radial axis as:

$$-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = m\left(-\frac{v^2}{r}\right)$$

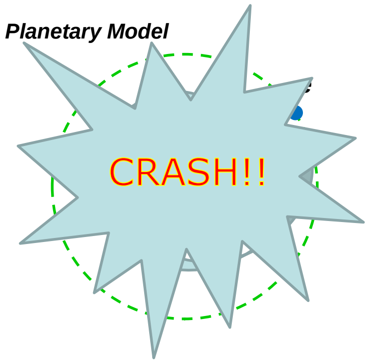
where m is the electron mass

$$r = \frac{e^2}{4\pi\varepsilon_o m v^2}$$

Orbit radius r calculated this way can take any value, nothing suggest at this point that it should be quantized!

5.2. Early models of atoms

Failure of the classical (planetary) atomic model



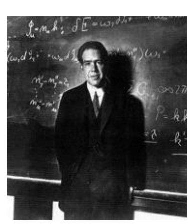
The electron is attracted by the nucleus. Even in circular motion around the nucleus, the electron loses energy:

- Radial acceleration: $a_r = v^2/r$
- Classical electromagnetic theory predicts that an accelerating charge continuously radiates energy, **r decreases**…

The electron would eventually crash into the nucleus !!!!!

5.3. The Bohr model

The Bohr theory of hydrogen atom



Niels Bohr (1885 - 1962)

In 1913 Niels Bohr creates a model that includes both classical and non-classical (quantum mechanics) ideas and attempts to explain why hydrogen atom is stable.

The most important postulate of Bohr model is that the electrons may be in stable (non-radiating) circular orbits, called stationary orbits. Electrons in states corresponding to the stationary, allowed orbits have their angular momentum L restricted to some discrete values being the integer multiple of the Planck's constant:

$$L = n\hbar \qquad n=1,2,3.....$$

5.3. The Bohr model

Postulates of Bohr model:

1. Atoms can exist only in certain allowed „states”. A state is characterized by having a definite (discrete) energy, and any change in the energy of the system, including the emission and absorption of radiation, must take place as transitions between states

2. The radiation absorbed or emitted during the transition between two allowed states with energies E_1 and E_2 has a frequency f given by

$$E = E_1 - E_2 = hf$$

$h = 2\pi\hbar$ is the same constant that appears in the treatment of blackbody radiation

5.3. The Bohr model

Postulates of Bohr model (continued)

3. Some of the allowed states – the ones that correspond to the classical circular orbits – have energies determined by the condition that their angular momentum is quantized as an integral multiple of Planck’s constant ħ

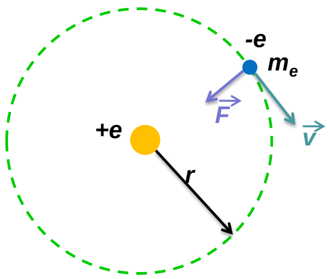
$$L = n\hbar$$

$$n = 1,2,3.....$$

The integer *n* will be reflected in all atomic properties. We call this integer a quantum number.

5.3. The Bohr model

Illustration for hydrogen atom

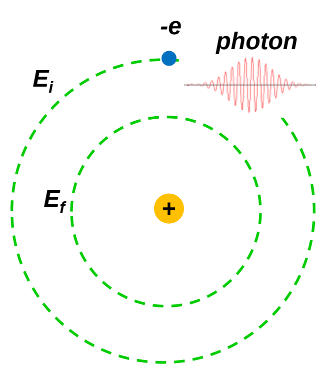


According to Bohr's atomic model, electrons move in definite orbits around the nucleus, much like planets circle the Sun. These orbits, or energy levels, are located at certain distances from the nucleus – orbit radius.

5.3. The Bohr model

Bohr's Quantum Conditions

There are discrete stable states for the electrons. Along these states, the electrons move without energy loss.
The electrons are able to "jump" between the states.



In the Bohr model, a photon is emitted when the electron drops from a higher orbit (E_i) to a lower energy orbit (E_f).

$$E_i\text{-}E_f=hf$$

5.3. The Bohr model

Orbit Radius

Orbit radius can be calculated:

The angular momentum is:

$$L = |\vec{r} x \vec{p}| = mvr\sin(\varphi)$$

where φ is the angle between momentum *p* and radius *r;*
here φ=90^0

$$mvr = n\hbar \; with \; n = 1,2,3 \ldots$$

velocity of the electron is: $v = \frac{n\hbar}{mr}$

5.3. The Bohr model

Orbit Radius

$$-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = m\left(-\frac{v^2}{r}\right) \Leftarrow v = \frac{n\hbar}{mr}$$

$$\Downarrow$$

$$\boxed{r = \frac{4\pi\varepsilon_0 h^2}{me^2} n^2 = n^2 a_0}$$ for n=1,2,3,...

a_0 - Bohr radius

$$a_o = \frac{h^2\varepsilon_o}{\pi me^2} = 52.92\ pm$$

Diameter of the hydrogen atom:

$$d = 2r = 2a_0 \approx 10^{-10}[m]$$

5.3. The Bohr model

The energy E of the hydrogen atom is the sum of kinetic K and potential U energies of its only electron

$$E = K + U$$

$$\Downarrow$$

$$E = \frac{1}{2}mv^2 + \left(-\frac{1}{4\pi\varepsilon_o}\frac{e^2}{r}\right) \Leftarrow -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = m\left(-\frac{v^2}{r}\right)$$

$$\Downarrow$$

$$E = -\frac{1}{8\pi\varepsilon_0}\frac{e^2}{r} \Leftarrow r = -\frac{4\pi\varepsilon_0 h^2}{me^2}n^2$$

$$\Downarrow$$

5.3. The Bohr model

$$\Downarrow$$

$$\boxed{E_n = -\frac{me^4}{8\varepsilon_0{}^2h^2}\frac{1}{n^2}\ for\ n = 1,2,3\ldots}$$

The orbital energy E_n is quantized

The negative sign indicates that the electron is bound to the proton

$$E_n = -\frac{2.18 * 10^{-18}[J]}{n^2} = -\frac{13.60[eV]}{n^2}$$

n=1: ground state, i.e., the lowest energy orbit of the hydrogen atom

5.3. The Bohr model

Specific Energy Levels

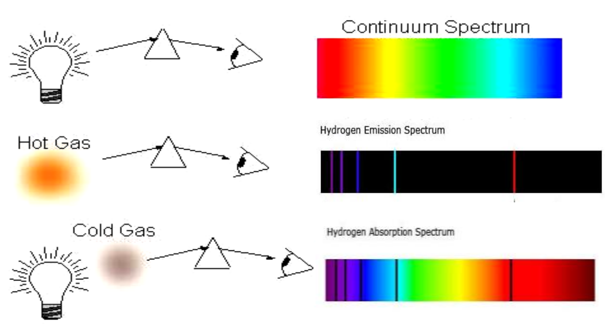
The lowest energy state is called the *ground state*
- This corresponds to $n = 1$
- Energy is −13.6 eV

✓ The next energy level has an energy of −3.40 eV
- The energies can be compiled in an *energy level diagram*

✓ The *ionization energy* is the energy needed to completely remove the electron from the atom
- The ionization energy for hydrogen is 13.6 eV.

5.4. Atomic spectra

Emission and absorption spectra



A white light (all visible frequencies) spectrum is observed as a continuum spectrum.
In the emission spectrum characteristic lines are observed.
In the absorption spectrum the absorbed characteristic lines are observed as a black lines on the continuum spectrum background.

5.4. Atomic spectra

Hydrogen atom cannot emit or absorb all wavelengths of visible light. Well before the Bohr formulated his model, Johann Balmer, by guesswork, devised a formula that gave the wavelength of emitted lines.

Later on, Bohr has rewritten his expression for quantized energy of hydrogen atom to get exactly the same formula

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{n_{\mathrm{f}}^2} - \frac{1}{n_{\mathrm{i}}^2}\right)$$

Paschen series, $n_f = 3$, $n_i = 4,5,6,\ldots$ infrared
Balmer series, $n_f = 2$, $n_i = 3,4,5,\ldots$ visible
Lyman series, $n_f = 1$, $n_i = 2,3,4,\ldots$ ultraviolet

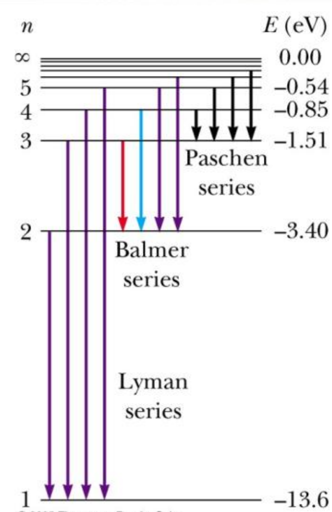
5.4. Atomic spectra

Energy Level Diagram

Rydberg constant

$$R_H = \frac{me^4}{8\varepsilon_0{}^2 h^3 c} = 1.097 * 10^{-7}\left[\frac{1}{m}\right]$$

- The value of R_H from Bohr's analysis is in excellent agreement with the experimental value
- A more generalized equation can be used to find the wavelengths of any spectral lines



Bohr's Correspondence Principle

Bohr's *Correspondence Principle* states that quantum mechanics is in agreement with classical physics when the energy differences between quantized levels are very small

Similarly, the Newtonian mechanics is a special case of relativistic mechanics when v << c

Conclusions

The Bohr model was a big step towards the new quantum theory, but it had its limitations:

- it works only for the single-electron atoms
- does not explain the intensities or the fine structure of the spectral lines
- could not explain the molecular bonding