

# **Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) for Pollution Monitoring**

**Dr. J R Mudakavi**  
**Department of Chemical Engineering**  
**Indian Institute of Science, Bangalore**

## **Lecture – 04** **Course introduction and atomic structure – IV**


Continuing our discussion our modern atomic theory in recent years has a highly mathematical character.

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**Modern Atomic Theory**

Modern atomic theory in recent years has a highly mathematical character and several physical and characteristics can be derived from our current understanding of the atomic structure.

In simple terms the structure of the atom is based on Bohr-Rutherford theory that an atom consists of a large portion of unoccupied space but populated by revolving electrons around a positively charged, relatively stable nuclear mass called as nucleus which is composed of neutrons and positively charged protons.



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And the model basically is these structure of the atom; it is based on a Bohr Rutherford theory. So, it consists of a large portion of unoccupied space around the nucleus, but it is populated by revolving electrons around a positively charged dense, relatively stable nuclear mass called as nucleus which is composed of neutrons and positively charged protons.

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**The Atomic Nuclei**

Protons and neutrons together constitute the weight of element. The mass number is the whole number closest in magnitude to the actual weight (in AMU) of the element. Since neutron and proton differ by a unit charge we may write,

$$\text{Neutron} \xrightleftharpoons[e^-]{e^+} \text{Proton}$$

However this equation represents an over simplified case. The small masses of electron and positron forbid their functioning in such reactions.

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So, the atomic nuclei what do we know about them? The protons and neutrons together constitute what is known as the atomic weight or weight of the element. So, the mass number; these atomic mass unit there is no specific weight like that except that we have weighed approximately about  $10^{-24}$  grams or something, but the mass number is the whole number closest in magnitude to the actual weight in atomic mass units. So, everything is measured only in atomic mass units and since neutron and proton have the same atomic mass, but there is a difference of charge; proton has a positive charge and neutron has no charge.

So, if I take a neutron add an electron to this, I get a proton and if I take a proton remove an electron from that I get a neutron. So, this kind of equilibrium reaction can be happening in most of the proton neutron systems; however, the equation; what I have written here neutron plus electron go into proton. Proton minus electron go to neutron this equation represents an a very very simplified case and the small masses of the electron and positron actually if they permit their functioning in such reactions.

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In 1913, J.J. Thompson showed that Neon contains atoms of mass numbers 20 and very small fraction of mass number 22. Since the chemical properties of both atoms were exactly same, Soddy suggested the term 'isotope' for such elements meaning there by they occupy the same places in the periodic table. They are chemically identical and differ only in physical properties which are dependent upon the mass.

Elements of even atomic number are more abundant, more stable and richer in isotopes than the elements of odd atomic numbers.

Except hydrogen and tritium, neutrons and protons tend to be equal in all elements. Generally neutrons to proton ratios are around 1.2 but never exceed more than 1.6.



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So, in 1913, Sir J J Thompson showed that the neon contains the neon is a gas you.

Must have seen neon lights all around you in all shopping complex, etcetera very familiar chemical around us, it contains atoms of mass numbers 20, then very small fraction of 22. So, work continued on this then they said that a neon atom has got 2 types neon gas, some atoms have a atomic mass unit of 20 and very small portion of that is having mass of 22; that means, there are 2 types of neon having a different number of protons because chemically if they have to be differ, if they have to be same the protons have to be same, but the mass that pre sit in protons, then neutrons are equal, then there should not be any difference at all.

So, if you determine the average weight of a neon you will end up somewhere between 20 and 22 you will neither get 20 nor 22; that means, there is small amount of a neon contains elements having mass number 22. So, chemical reactions are same; isn't it? So, chemical properties of both the atoms are same. So, Sody suggested another scientist called as Sody he suggested a term known as isotope he said if the chemicals are same if the chemical properties are same the only difference is in the physical characteristics. So, if the physical characteristics are different chemically they are same it is just like having a one person.

Having twins both of them look alike, but they are different. So, the he suggested a term known as isotope for such elements which are having different mass numbers, but same

chemical properties. So, they occupy the same places in the periodic table because a periodic table nowadays is based on the atomic number that is number of protons rather than the atomic mass we will study about it a little bit later. So, they are all chemically identical and differ only in physical properties which are dependent upon the mass. So, if there are elements having different atomic mass.

If there are elements having different atomic mass some are more abundant some are less abundant and some are more stable and richer in isotopes some are less stable. So, the question arises whether such elements are stable or not. So, the elements; the fundamental principle is elements of having even number of protons and even number of neutrons. So, elements of even atomic numbers are normally more abundant; that means, 2, 4, 6, 8 like that atoms elements they are more abundant than odd numbers elements of odd number that is 1, 3, 5 like that.

And except hydrogen and tritium a tritium is an isotope of hydrogen having 2 neutrons and 1 proton hydrogen is one proton no neutron. So, except hydrogen and tritium neutrons and protons tend to be equal in all elements that is the bottom line. So, if you take any element the number of protons and number of neutrons tend to be approximately equal generally neutron to proton ratios are around 1.2, it is not exactly 1.0, but around 1.2, but they never exceed more than 1.6; that means, the isotopes are never more than 50 percent in any element.

So, this is a point to be noted for our general discussion because it may have some implication in the spectroscopic interpretation. So, what he suggested Soddy he suggested that there are nuclei with even number of neutrons and equal number of protons such nucleus are most abundant than those of odd numbers even number nucleus and protons and neutrons elements are more abundant than the odd number of neutrons.

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- Nuclei with even number of neutrons are more abundant than those of odd number of neutrons.
- Nuclei with even mass numbers are more stable than the nuclei of odd numbers.

Early mass spectrographic data of hydrogen indicated that its atomic weight is 1.007775 based on the assumption that ordinary oxygen is not an isotopic mixture and has an atomic weight of 16.0000. This value was acceptable because 1.00778 grams of hydrogen combines with 8 grams of oxygen. However subsequently oxygen isotopes of 16, 17 and 18 mass numbers were discovered. Therefore two types of mass numbers are in use. One refers to chemical atomic weight of 16.00000 and the other known as physical atomic weight refers the average atomic weight of 16.00447. The former is universally accepted for the routine purposes and the physical values are used to describe the properties related to atomic nuclei.

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So, nuclei with even mass numbers are more stable than the nuclei of odd numbers. So, now, I think you are able to understand concentrate understand that we are discussing only about the nucleus not the electrons. So, early mass spectrographic data of hydrogen people looked at it very easy very consistently and its atomic weight was confirmed to be 1.00 double triple 7 5 based on the assumption that ordinary oxygen is not an isotropic mixture, but it has an atomic weight of 16. This is a reference value for us, it means you want to compare the weight of any element you take oxygen as standard the average weight atomic weight is 16 provided oxygen does not have any isotopes.

This value was acceptable and it became if you take this value then the weight of one hydrogen atom is approximately 1.00778; that means, now you imagine the 8 grams of oxygen, one gram of hydrogen will combine with 8 grams of oxygen and the oxygen isotopes, there are 3; one with 16, 17 and 18 mass numbers, they are already there; there for 2 types of mass numbers are in use one refers to the approximate average weight of 16.0000 whatever it is for reference and the other which is known as for actual calculations.

That takes into account the isotopes that average weight is 16.00447 for theoretical for calculation of very high accuracy we take atomic weight of oxygen is 16.00447 and for normal routine work we take it as 16.0000 that is 5 decimals the former is usually accepted for routing purposes and the physical values are used to describe the properties

related to atomic nuclei. So, nuclear stability again, we have been discussing about it the presence of stable elements implies that neutrons and protons are held together by attractive forces.

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### Nuclear Stability

The presence of stable elements implies that neutrons and protons are held together by attractive forces. At the same time coulombic repulsive forces must also be present. The sum total of these forces would be attractive forces.

The energy exchanges between the protons and neutrons would be maximum when equal number of the neutrons and protons exist. Therefore for better stability, N:P ratio should be unity.

However since protons mutually repel each other, a tendency to repel each other also exists. For elements containing a few protons and more neutrons, there is a tendency towards equalization of protons and neutrons.

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We are discussing about nuclei nucleus there are protons there are neutrons.

And these are held together by attractive forces at the center of the atom at the same time the coulombic repulsive forces also must be present. Now I want you to understand the concept here we are talking about the nucleus. Nucleus has got protons and neutrons protons have positive charge neutrons do not have any charge, but still they are all together; that means, the fundamental law of physics is any substance which has a weight must exert some sort of a force that is known as the attractive force anything that ways.

So, the protons and neutrons must be attracted together into each other to remain together at the center of the nucleus these are known as coulombic forces. So, the coulombic forces repulsive forces are there they also must be present coulombic forces can be attractive as well as repulsive so, but still all around us we see that the nucleus is stable; that means, the positive charge the sum total of the forces would be attractive forces because this stay together. So, the repulsive forces generated by the mass of protons and neutrons are overtaken by the attractive forces between the between the nucleus and protons that is how the protons and neutrons stay together at the center of the atom.

So, the energy changes between the protons and neutrons would be maximum energy exchanges when equal number of neutrons and protons are exists; that means, the electrons and protons if they are equally numbered the energy change between the 2 would be equal and it will be more stable. So, for better stability of a nucleus the neutron to proton ratio should be unity if they are equal it will be unity if they are not equal it will not be unity it will not be so stable as the one with equal number of protons and neutrons; however, since protons usually a mutually repel each other protons also if you bring any 2 protons you know both positive you try to bring them together. So, like forces repel each other.

So, 2 positively charged protons also would repel each other right. So, a since protons mutually repel each other a tendency to repel other also should exist in the nuclear force in their nucleus. So, for elements containing less protons and more neutrons there would be a tendency towards equalization of protons and neutrons you try to understand. This concept protons also repel each other, but if there are more protons if there are more protons and less neutrons there is a tendency towards equalization and the other way also if there are less protons and more neutrons again there is a tendency.

So, such elements would be having some sort of a stability problem and they would like to move to stable composition and that is how the radio activity also is a very important phenomena especially when high molecular high atomic weight molecule elements are there they try to acquire stable nuclear mass having equal number of protons and neutrons.

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The atomic weights of the elements show remarkable constancy indicating that the isotopic composition remains constant on the earth. Only oxygen shows higher abundance of heavier isotopes in the atmosphere than water. Further variations in the atomic weights are generally noticed for heavy elements due to their radioactive origins.

Another factor affecting the nuclear stability is the sheer mass of the nucleus. Nuclei possessing excessive mass (above 209) are spontaneously unstable. Such nuclei re-adjust themselves by emitting  $\alpha$  particles (Helium atoms,  ${}^4_2\text{He}$ ) which decreases the atomic weight by 4 amu and atomic number by 2.

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So, the atomic weight of the elements show remarkable constancy indicating that the isotopic composition remains constant on the earth. This is a very important fundamental rule that is atomic weights of the elements show a remarkable tendency for isotopic composition it should be constant all over the earth whether it is in gaseous form or solid or liquid form either way.

So, only oxygen shows higher abundance of heavier isotopes in the atmosphere than water you know as we all know that water is a very important concept in the environment right. So, water is having hydrogen, oxygen and deuterium oxygen tritium oxygen. So, any water that you have would be having all the 3 and then only the oxygen also has a higher abundance of isotopes. So, wave oxygen shows higher abundance of having their isotopes in the atmosphere than water because water is less in quantity on the surface of the earth than oxygen. So, further variations in the atomic weights are normally noticed for heavy elements due to their radioactive origins.

So, the factor that affects the nuclear stability is basically the sheer mass of the nucleus only nuclei processing excessive mass that is I just now mentioned that heavier elements. So, the heavier elements means what is the limit of heavy element we say approximately 209 to above that we call it heavier elements.

And then there are spontaneously unstable and try to achieve nucleus stability by emitting alpha particles that is helium atoms to achieve 4 helium atoms with 2 atomic



charge and 4 mass atomic mass emits. So, they elements heavier than 209 atomic weight keep on losing the helium atoms that decreases their atomic weight by 4 a m u and atomic number by 2 it reduces; that means, the product after losing alpha particle is lighter in weight by 4 units and lighter in atomic number by 2 units.

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**Nuclear Reactions**

Various processes involved in such reactions are classified as :

- Capture reactions
- Particle-particle reactions
- Fission reactions
- Spallation reactions
- Fusion reactions

All these reactions are in turn induced reactions which fall into five categories:

1. Alpha-induced reactions
2. Proton induced reactions
3. Deuteron induced reactions
4. Gamma induced reactions
5. Neutron induced reactions

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So, what are the how does it happen such elements lose they lose their atomic excess weight by various processes and such reactions are classified as capture reactions particle reactions fission reactions, spallation reactions and fusion reactions. So, all these reactions are intern induced reactions which fall into 5 categories, one is the alpha induced reaction; that means, alpha helium particles and you can they can be photon proton induced reactions and then they can be deuteron induced reaction and then neutrons that is gamma; gamma rays induced reactions and neutron induced reactions. So, all these are the mechanism through which the heavier element would keep on losing the excess weight by losing the electrons by losing the neutrons and protons to achieve the nuclear stability.

These are this kind of information is usually required for understanding of the atomic structure, but not for icp what for our course. So, we are not going into details of this, but stuff I said to say that there are nuclear stability issues and isotopes and such reactions such element having higher number of protons and neutrons tend to lose their excess weight by reaction with alpha that is helium atoms protons neutrons deuteron induced

reactions and gamma ray induced reaction they that these are the different reactions through which a heavier element tries to tries to attain the nuclear stability.

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In 1903, Bohr proposed a radically different view of the atomic structure based on the optical spectrum of Hydrogen. He included the postulates of quantum theory proposed by Max plank.

Bohr proposed that the electron in a hydrogen atom always described a fixed circular path around the nucleus. Such orbits named 'stationary states' may be thought of various circles differing in radius.

The angular momentum of each stationary states was an integral multiple of  $h/2\pi$  which amounts to angular momentum. The angular momentum ( $mvr$ ) is given by,

$$mvr = n(h/2\pi)$$

where 'n' is an integer called a quantum number.

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Now, what we have understood so far is that the atom as we understand today. It contains protons neutrons and electrons, there are other fundamental particles such as masons and then positrons neutrons anti neutrons and several other particles are there they do not have a specific existence and there are as far as we discussed about the stability of the nucleus with respect to the electrons what we generally conveyed so far in our discussion is that there are protons and neutrons in the nucleus and these are held together by colonic forces.

The sum total of the colonic forces is positive that is why they all stay together, but there are reactions there are forces which also repel each other. For example, 2 protons will should repel each other and then 2 neutron should repel each other because of the colonic forces and equations. So, in now, we are going back towards the electronic structure. So, in nineteen not 3 Bohr proposed a radically different view of the atomic structure which we have already seen earlier by a through a crude model and, but this time in Bohr proposed a structure for atoms based on the optical spectrum of hydrogen what he in did was the spectrum of hydrogen shows different lines and I will show you in my next class. The each line represents certain amount of transition of electron from one energy level to the next energy level what he did his greatest contribution is that the energy

corresponding to each transition what he said is based upon the exact quantity of energy that is not continuous; that means, every transition must require specific quantity or specific amount of energy and this is known as quantized energy.

I want you to understand that the quantized energy system is proposed by Max Planck that is based on the black body radiation and we are not going into details of that except to understand that the every energy transition in any element requires a specific amount of energy and the next transition would not be a continues increase in the energy, but another quantum of energy; that means, only when there is exact quantity of energy is supplied to the system the transition takes place otherwise it will not if you the; it is it goes by specific requirement of energy rather than continues increase of energy. So, Bohr proposed that the electron in a hydrogen atom always describes a fixed circular path that we have already seen around the nucleus.

So, such orbits are name as are known as stationary states and it may be sot of various circles depending in radius this we have already seen. So, if the electrons are there moving around the nucleus electrons are moving around the nucleus the electrons would be having some sort of an orbital angular momentum. So, they it is the moment of any electron going around the circle is governed by cetripitated force and centrifusel force and the that is how it is held in the position in around the nucleus otherwise it will either fall into the nucleus or it will go away from the new from the nucleus from its central path and we will be divide of any electrons, but it does not happen.

So, the angular momentum of the stationary states was an integral multiple of  $h$  by  $2\pi$  that  $h$  is known as Planck's constant this is how the quantum mechanical relationships enter into the atomic structure. So, each stationary state is state is defined by  $h$  by  $2\pi$  where  $h$  is known as Planck's constant, it amounts to the angular momentum the angular momentum is also given by mass into velocity into radius that is  $m v r$ , it is a multiple of  $n$  into  $h$  by  $2\pi$ . So,  $n$  cannot be a fraction according to the quantum mechanical this si the beauty  $n$  can be one it can be 2 it can be 3.

It can be 5, it can be any number, but it can be one point 2 or one point 5 or 2 point seven like that. So,  $n$  is an integer called as quantum number this as concept Bohr included in the atomic structure.

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He also postulated that as long as the electron remained in a given orbit it neither radiates nor absorbs energy.

When the electron moves from one orbit to another it was considered to involve the absorption or emission of definite quantity of energy depending upon whether the electron moved from lower state to higher one or vice versa.

This energy manifests as radiation and the frequency of such radiation is manifests a spectral line which could be related to the energies of electron in the two states  $E_1$  &  $E_2$ .

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He also postulated that as long as the electron remained in a given orbit it neither radiates energy nor absorbs energy this is a very important concept again . So, what he said is the electron goes round and round and round, but as long as it is stable in that along is it retained it is remaining in the orbit it does not lose energy or does it gain energy it is does not absorb energy it does not lose energy.

So, when the electron moves from one point to another that is from one level to another level it has to it has to either absorb energy or it has to lose energy or emit energy. So, the amount of energy that is keep me on. So, the amount of energy that is retained in the either during absorption or emission must be equal to the quantum mechanical energy that is defined by  $mvr$  is equal to  $n h$  by  $2 \pi$  where  $n$  would be 1, 2, 3, etcetera not the fraction. So, it depends it is dependent upon whether the electron moves from lowest to higher energy state that is absorption of energy.

And if it is falling from higher energy level to lower energy it has to lose that much of extra energy. So, this is what it means the lowest state for to highest state and vice versa it can lose energy or it can gain energy. So, this energy difference occurring during absorption or emission, it manifest as radiation and the frequency of such radiation is the manifestation of a spectral line that you see in a hydrogen atom which could be related to the energy of the electron in each state that is you initial state and final state that I had designated here as  $E_1$  and  $E_2$ .

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**Line spectra of hydrogen atom**

Lyman series	$n = 2, 3, 4, \dots$ to $n = 1$
Balmer series	$n = 3, 4, 5, \dots$ to $n = 2$
Paschen series	$n = 4, 5, 6, \dots$ to $n = 3$
Brackett series	$n = 5, 6, 7, \dots$ to $n = 4$
Pfund series	$n = 6, 7, \dots$ to $n = 5$

**Origin of hydrogen spectrum**

Bohr's theory could explain the spectra of hydrogen and etc. But it failed completely when applied to multiple electron systems. Further it could not account for splitting of optical lines (fine structure) when spectroscopes of high resolving power were employed.

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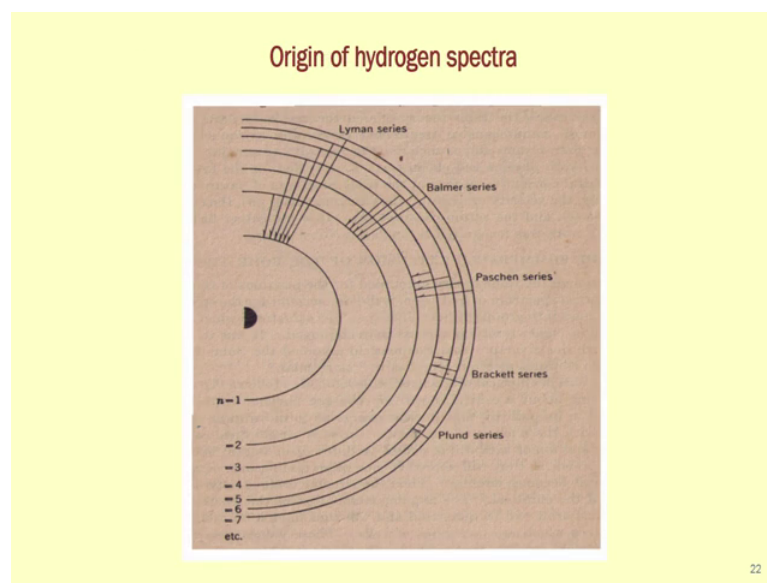
So, what he meant is that the line spectra of hydrogen atom is described by a number of series known as Lyman series, Balmer series, Paschen series, Brackett series and Pfund series. This Balmer series is a spectrum of hydrogen that is in the visible region that you can see the lines in a region where with our naked eye and Lyman series are a series of lines in the hydrogen spectrum which occur in the ultraviolet region and Paschen series occurs in the infrared region. Brackett series still lower down the energy that we will see later and Pfund series is another series where you can see that here it is  $n$  is equal to 1 and  $n$  is equal to 2 and  $n$  is equal to 3, 4, 5, etcetera and the transition occurs from 1 to 2, 1 to 3, 1 to 4 like that for in Lyman series transition occurs from 2 to 3, 2 to 4, 2 to 5 like that in the for the Balmer series 3 to 4, 3 to 5, 3 to 6 like that you will end up with the number of lines in a hydrogen spectrum and each line can be ascribed to one of these transitions. So, the origin of hydrogen spectrum is that it could explain the spectra of hydrogen.

And, but it failed completely when applied to multiple electronic systems for actually I have been describing this only for hydrogen atom. So, hydrogen atom has got only one proton and one electron you excite that electron to higher energy level according to Bohr's theory from one energy another energy the difference is fixed and constant. So, if the bottom line is number one and next energy is this 2, 3, 4, etcetera, there you will see number of lines corresponding to 1 is to 2, 1 is to 3, 1 is to 4, 1 is to 5 like that that is

Lyman series and still I come to slightly higher energy level 2 to 3, 2 to 4, 2 to 5 like that you will see Balmer series then Paschen series 3 to 4, 3 to 5, 3 to 6, etcetera.

So, this Bohr theory could explain most of the lines for hydrogen atom, but not for higher elements that is helium lithium ion cobalt and all they all became very complicated you cannot really ascribe each element because it is almost impossible task to imagine all the line spectra and assign it to specific energy level. So, this Bohr's theory could not explain the spectra of hydrogen it could explain the spectra of hydrogen because it is a simple system, but it fail completely when apply to multiple electron systems helium lithium beryllium boron carbon and all those things. So, further it could not account for splitting the for oxygen optical lines when spectroscopy spectroscopes of high reasoning power were employed. So, that is the crux of the problem.

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So, this is the pictorial representation this is Lyman series one this is there from here to here; this is the first circular orbit. So, 2 to 1, 3 to 1, 4 to 1 like that; it can be is other way also 1 to 2, 1 to 3, 1 to 4 like that this is all Lyman series. This is all Balmer series, they all end up with 2, they do not go to one. So, the all the transitions are from higher level to lower level energy level this is for emission and same thing is true with Paschen series bracket series and fund series. So, this is the origin of line spectrum etcetera and spectroscopes of higher energy level.

What happens; this is if any line in high resolution spectrum instead of showing why up 4 it should show 8 or 10, then we do not know how to interpret. So, the Bohr's theory could not explain the extra lines that appear when spectroscopes of high resolving power were employed. So, that is where the failure of Bohr's orbit Bohr's theory and then there were some slight improvement in the understanding of the atomic structure using by Sommerfeld theory that we will see in the next class.