Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 04
Electronic arrangement in the Elements

In 1916 Sommerfeld modified Bohr's theory; to include elliptical orbitals. Earlier I had said that the electrons will move around circular orbits; now we do not say that the orbitals are circular around the nucleus they are elliptical. So, sometimes just like sun and moon as they come nearer the earth they look bigger and when they go far away they look smaller similarly electrons in an around the nucleus will follow a circular path.

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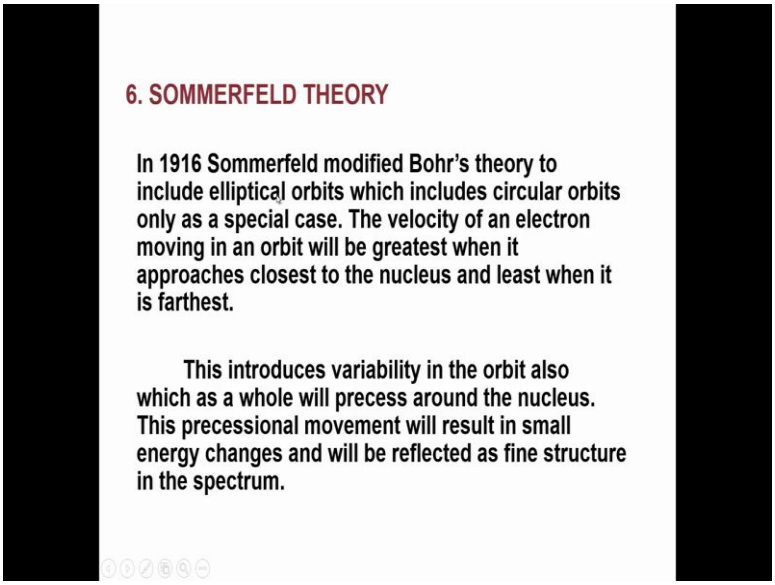

So, this he included electrical orbitals that also includes circular orbit as a special case. So, I think if you have studied pre university chemistry, you will know that elliptic circular orbits are a special case of elliptical orbital's orbits.

So, when a there are 2 axis one is a and b when a and b are equal it is circular orbit. If when they are not equal it is an elliptical orbit. So, the velocity of an electron moving in an orbit will be greatest if it is nearer the nucleus. So, when the sun is, when full moon is there the attraction of the full moon towards earth is more bigger, similarly that means, the attraction is more velocity also will be more. So, it approaches closest to the nucleus the velocity is maximum, and then when a velocity is very less then it is further away;

this introduce is a very variability in the orbit also which as a whole will process around the nucleus keeps on going like this and the this processional movement will result in small energy changes and this will be reflected as fine structure in the spectrum; this spectrum was not shown in the earlier orbit Bohr's theory.

What Bohr's said they go around stationery nucleus stationery circulars, and now you are saying elliptical orbit there are in the elliptical orbits when it is nearer the nucleus the speed should be more when it is further away the speed should be less, and when we this increase and decrease in the speed will result in fine structure of the spectrum when we record it.

So, this is reflected as a fine structure, in Bohr's structure theory such fine structures were not visible; that means, the Sommerfeld theory explains the small structures of the features of the spectrum.

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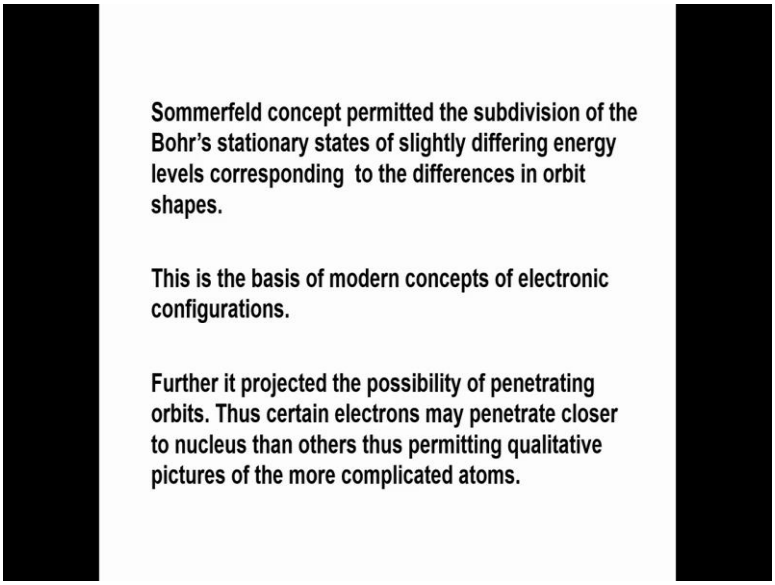

So, this permitted the subdivision of Bohr's stationary states a slightly different energy levels corresponding to differences in orbital shapes. Now every element we know has got number of electrons around it and then the fine structure of every element is different.

Now, this fine structure is what we are going to use in atomic absorption spectrometry that is why I am taking so much of time to explain the electronic structure. So, it is the

Sommerfeld theory also project in the possibility of penetrating orbits. See imagine here is a nucleus electrons are going around, this around the space is empty. So, like this one this is one orbital this is another orbital they can interact inter space, now they are not independent one is here another is here another is here like that no it does not work, the orbitals can be interspaced. Just like a woman wearing a bangle all over the bangles can overlap one another, the orbitals also overlap one another. So, this certain electrons may penetrate closer to nucleus than other electrons which are not closer.

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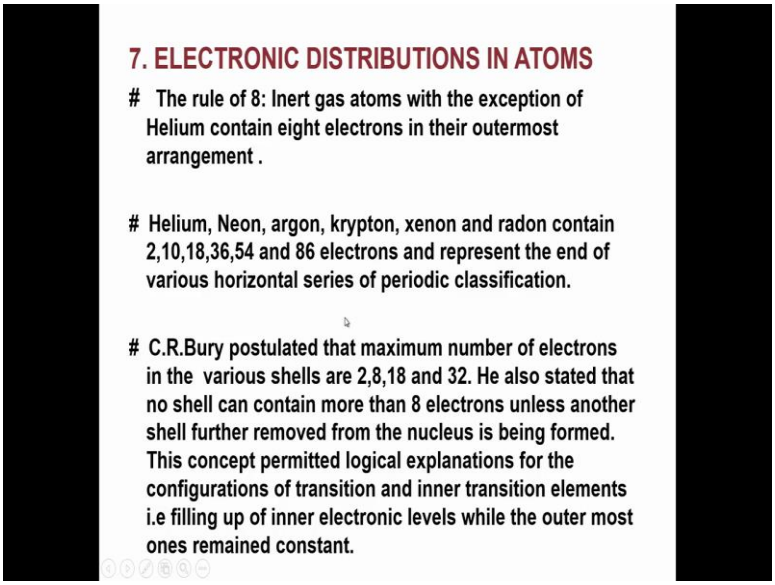

So, how do we assume that the electrons are dispersed in a an atom; the electrons some of them may be nearer the nuclear some of them may be the far away from the nucleus, but still there is a certain amount of law certain laws they have to follow what are those laws? There is a rule of 8 inert gas atoms with exception of helium they must contain 8 electrons in their outermost orbit. So, this is known as rule of 8 that means, the in the now outermost orbit there cannot be more than 8 electrons; helium, neon, argon then krypton, xenon and radon they contain number of electrons 2, 10, 18, 36, 54 and 86 electrons, but in their last orbit all these elements contain 8 electron except helium that is number 2.

Now, C. R. Bury postulated that maximum number of electrons in the various shells are 2, 8, 18 and 32. He also stated that no shells shell contain more than 8 electrons unless another shell further removed from the nucleus is being formed. This concept permitted

logical explanation for the configurations of transition and inner transition elements that is filling up of inner electronic levels while the outermost once remain constant. So, we will come back to this when we study further.

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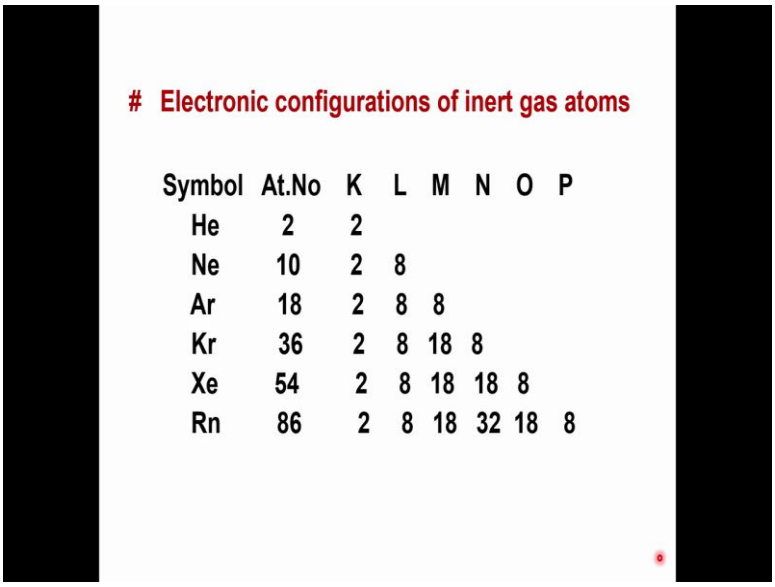

Now, the electronic configuration, electrons are arranged in number of orbitals orbits like K L M N O P and this is the helium, helium has got atomic number of 2 and then the all the 2 electrons are in the K shell. Neon contains 2 and 8 argon, argon has got 18 electrons and the electronic arrangement is 2 in K, 8 in L, 8 in M shell similarly krypton 2 8 18 8. Xenon will have 2 8 18 8 18 18 and 8 and radon will have 2 8 18 32 18 and 8. So, we can see that the last orbit in all these elements contain 8 electrons that is the rule of 8, and then maximum number of electrons can be 2 (Refer Time: 08:16) can have other electrons in inner shells they may be in accommodate inside and minimum is 2 ok.

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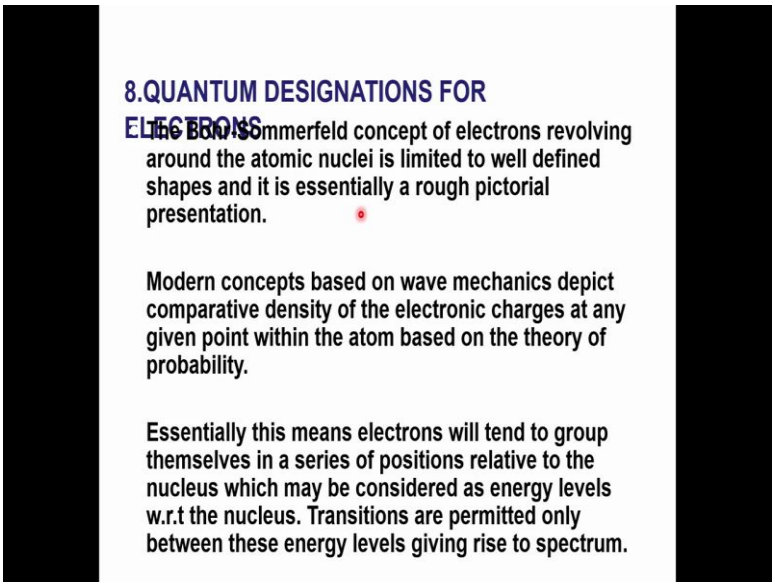

Now, quantum designations for electrons; this slide is slightly overlapping and what I can tell you at this stage is I can take it make it look a little better - the quantum designations of for electrons. Now we go back to the Bohr's Sommerfeld concept of electrons revolving around the atomic nuclei that is limited to well defined shapes and it is essentially a rough pictorial presentation. So, modern concepts based on wave mechanics depict comparative density of the electronic charges at any given point within the atom based on the theory of probability.

Now, you can say that the electrons are all fixed in a particular orbit; now what we are saying a further modification using quantum mechanics is that at any point in space the electronics the electron density at a particular space is determined by the wave mechanics and the wave mechanics can exactly describe what is the atomic density around the nucleus at various spaces space points around the nucleus. So, that is what this slide means; within the atom based on the theory of probability because the we say electron is in a constant state of motion and at any particular time it may occupy a space particularly at a particularly at a time and it may spend more time in a particular space than all over uniformly, that is what the wave theory wave mechanics in general depicts.

Now, essentially this means the electrons will tend to group themselves in a series of positions, relative to the nucleus which may be considered as energy levels with respect to the nucleus.

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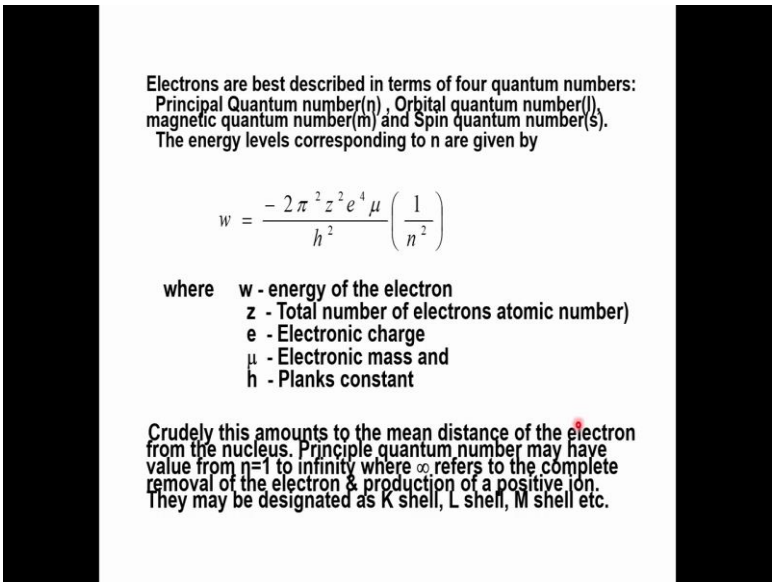

So, transitions are permitted only between these energy levels giving rise to the spectrum; that means, what we are essentially saying is the electron groups themselves in different areas and transitions between one position in the space to another position in the space is limited to the energistics. So, electrons are best described in terms of 4 quantum numbers.

Now, what are those 4 quantum numbers? One is principal quantum number n, second is orbital quantum number l, and third is magnetic quantum number m, and fourth is spin quantum number s. The energy levels corresponding to a particular electron in an orbit n is given by w is equal to minus 2 pi square z square e to the power of 4, and then electronic mass that is mu and then the planks constant. So, w is the energy of the electron, z is the total number of electrons that is atomic number same as atomic number e is the electronic charge, e raise to 4 is there mu is the electronic mass and h is planks constant.

So, crudely this amounts to the mean distance of the electron from the nucleus average distance. Principal quantum number may have value from n into 1; n is equal to 1 to infinity where infinity refers to the complete removal of the electron, it does not mean an electron position from the nuclear to infinity no it refers to the position of the electron around the nucleus where it is completely removed from the influence of the nucleus that is what it means. So, and when you remove an electron it produces a positive iron. So,

that is the point at which infinity is defined, they may be designated as K shell L shell M shell etcetera.

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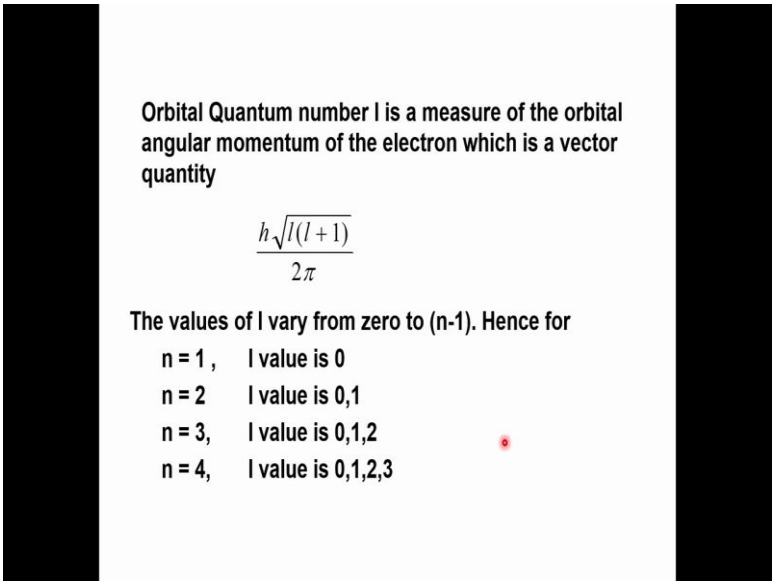

So, orbital quantum number l is a measure of the orbital angular momentum because electron is processing around the nucleus. So, the orbital angular momentum is nothing, but a particular number at which the electron distance in extra minutes or whatever it is away from the nucleus and in that area it is processing. So, the orbital angular momentum of the electron is given by this equation that is h is equal to l square root of l into l plus 1 divided by 2 pi. So, values of l vary from 0 to n minus 1. So, if n is equal to 1, n minus 1 is 0; and if n is equal to 3 it n minus 1 would be 2. So, 3 2 like that the value of l will be for n is equal to 1, l is 0 n is equal to 2 value of l is 0 and 1, n is equal to 3 it can be 0 and 2 like that the orbital angular momentum values quantum values will also change.

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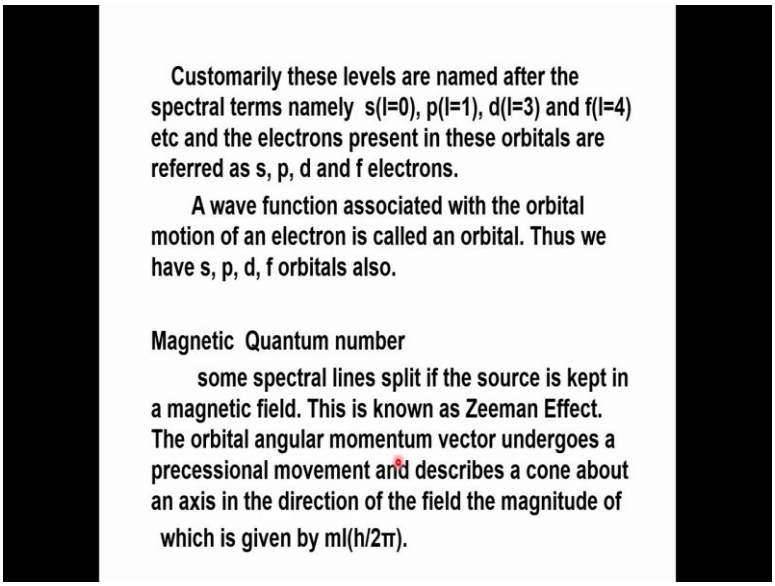

So, customarily these levels are named after spectral terms namely s is p d and f, when l is equal to 0 we call it s, orbital when l is equal to 1 we call it p orbital, l is equal to 3 it is d orbital l is equal to 4 it is f orbital etcetera; an you do normally you do not come across more than s p d and f electrons f orbitals and the electrons present in these orbitals are referred to as s p d and f electronic that is very simple to understand know. So, wave equation wave function associated with the orbital motion of an electron is called an orbital.

So, we have the apart from the electrons being referred to as s p d and f electrons, we also referred the orbitals as s p d and f. So, s orbital could be spherical in shape, p orbital could be dumbbell in shape and different shapes are also there I can show you some of them later maybe here I do not know where it is yeah here.

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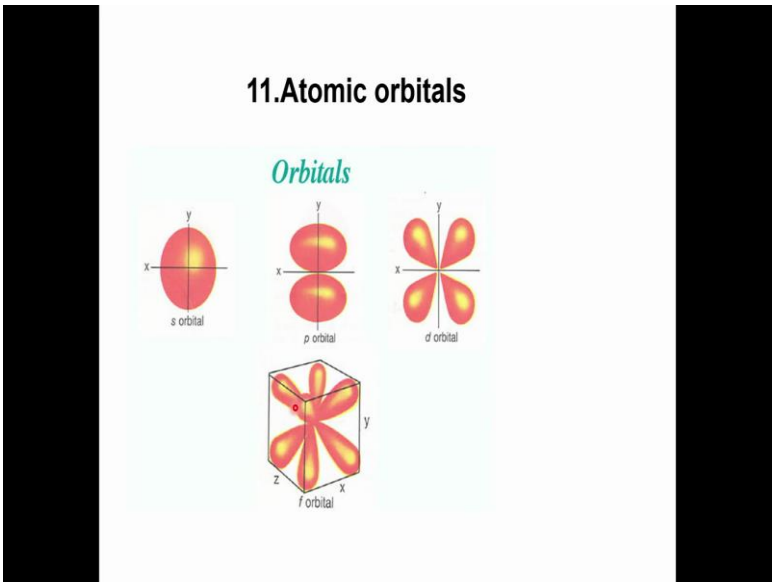

I can show you this is s orbital that is spherical in nature electrons present in s orbital are called as s electrons; here it is p orbital it is a dumbbell shape so that means, the electronic electron density along x axis is very less, here it is uniform all around the nucleus, you have to imagine that the nucleus is at the centre of the x y intersection of the x y, and herely similarly in p orbitals the electron distribution is above and below the x axis. Now we have d orbitals here the electrons are situated in the space between x and y and z also. So, these are planar basically x y z d orbitals where as f orbitals are 3 dimensional space they are all distributed in the 3 dimensional space ok.

Now, here I can also describe another magnetic quantum number that is magnetic moment quantum number. The reason for this definition of the magnetic quantum number is because some spectral line split if source is kept in a magnetic field instead of one spectral line you will see 2 spectral lines that is known as splitting. In the absence of a magnetic field you will see only one spectral line; whereas in if the put the same substance in a magnetic field you will see 2 spectral lines. So, the 2 spectral; that means, the magnetic field has got certain effect on the energetics of the electron. So, this is known as Zeeman Effect. So, the Zeeman is the gentleman who discovered this property of the electrons behave electron behavior in a spectrum so that we will be talking about Zeeman Effect atomic absorption later in the course.

The orbital angular momentum vector usually undergoes a precessional movement as usual and describes a cone like this if you can see the orbital angular momentum like this; you like this it will be rotating like this (Refer Time: 20:09) like this, it will be defining a cone. So, it describes a cone about an axis in the direction of the field in which the magnetic field is setup. So, this momentum is given by m l into h by 2 pi. So, m is the magnetic field.

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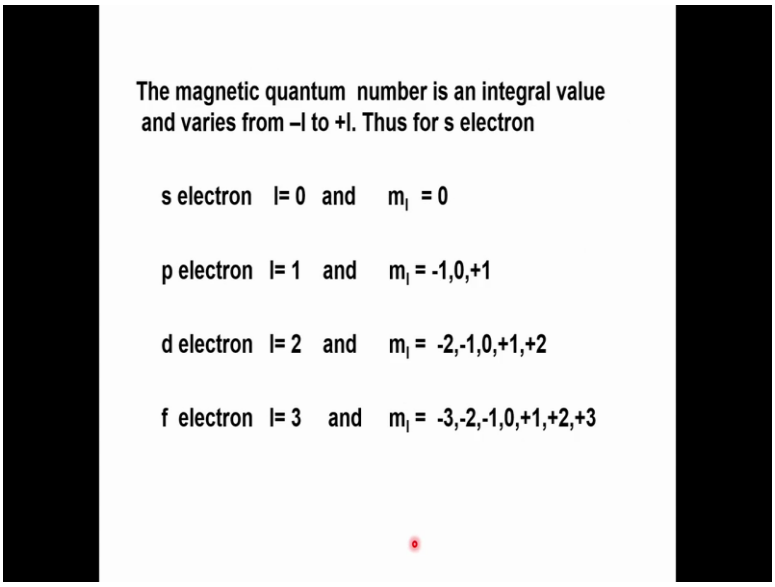

So, the magnetic field quantum number is an that is also an integral value and where is from minus l to plus l. So, for s electron l is 0 and magnetic momentum m l is also 0 because it is spherical in shape it has no effect of the magnetic field. For p electron l is 1 and m can have values of minus 1, 0 and minus 1 plus 1. So, for l is equal to 1 it is 3 energy states corresponding to different magnetic fields. Similarly for the d electron l is 2, and magnetic quantum numbers would be minus 2, minus 1, 0, plus 1, plus and plus 2; minus l to plus l. So, if it minus 2 it has to be the other parts should be plus 2.

So, minus 2, 1, 0 and then correspondingly plus 1 and plus 2, similarly for f electron it can be minus 3, minus 2, minus 1, 0, and plus 1, plus 2, plus 3 energy states. So, this is about the magnetic quantum number of an electron.

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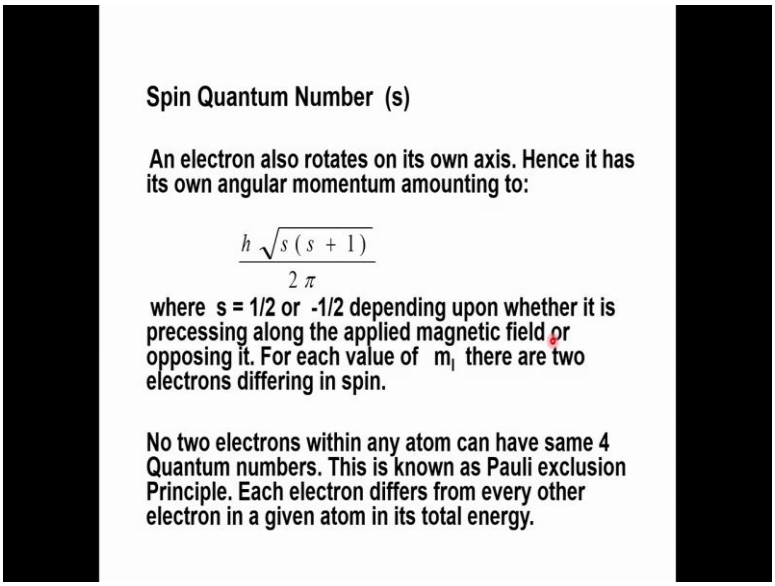

Now, we describe another quantum number corresponding to an electron that is designated as s that is spin quantum number. Now an electron can rotate apart from the nucleus it can it will be going round and round the nucleus, but it will also be going round and round itself. So, you can imagine that you are going around a temple where the statue is in the middle you are going round and round, but you are also revolving and then going round and round round round. So, that is how the spin quantum number was spin quantum number s is imagined, you can imagine that you are also turning and you are turning as well going round and round.

So, you can there can be only 2 directions you can turn either in the positive clockwise or anticlockwise there are no other combinations possible for the electron to go around itself right. So, it has to be either clockwise or anticlockwise so, but we have no way of determining how whether an electron is going in a clockwise direction or anticlockwise we cannot define it is only a relative term. Just like you are seeing my right hand on the on the screen my right hand is actually coming on the left side of the screen, similarly an electron it is only our imagination, how we define an clock wised spin or anticlockwise spin for an electron.

So, anyway the spin quantum number the spin angular momentum of an electron is given by h into square root of s into s plus 1 divided by 2 pi. So, where s the value of s can be plus half or minus half it cannot be anything in between or it cannot be anything more or

less. So, depending upon whether it is processing along the applied magnetic field or opposing it. So, it can be as I explained to you it is only a relative term; for each value of m 1, m, m there are 2 electrons differing in spin; that means, m is equal to 0 magnetic field we go back to the previous this thing for if l is equal to 0, m l is equal to 0; that means, there can be 2 electrons in this orbit ok.

Similarly, in p electrons there can be 2 here, 2 here, 2 here total 6 electrons. Similarly d electron will have 2 2 2 2 2 that is 10 electrons and this can be 14 electrons like that in each orbit there can be 2 electrons. So, 2 both electrons will be differing by a quantum number essentially one and half minus half. So, if we take a look at the quantum number of the electron in a given element, each electron will have main quantum number, the principal quantum number and then orbital angular moment quantum number and then magnetic quantum number and spin quantum numbers.

So, an electron can have the same principal quantum number, it can have same electronic same orbital angular momentum quantum number it can have the same magnetic momentum quantum number, but it cannot have the same electronic quantum number because there are only 2 electrons in each orbitals and the 2 electrons cannot be processing around each other if they are processing in the same direction, they have to be in the opposite direction then only an electron in an orbital can be safe; you understand the concept one both are negatively charged. So, they cannot be going cannot coexist together their paths momentum should match the attraction as well as repulsion of the electrons among themselves also. So, any electron in a given system cannot have does all the 4 same quantum numbers this is a fundamental rule.

So, the fundamental rule says every electron can be accounted by a set of quantum numbers which are not exactly same. So, it is like having a postal address for every person in your locality, at least the house number will be different; town maybe same, area maybe same, street number maybe same, but your house number will be different. So, like that every electron in every system will be having spin quantum number at least different from each other. So, no 2 electrons within any atom can have the same 4 quantum number, this is known as Pauli Exclusion Principle who proposed such a principle and each electron differs from every other electron in a given atom in its total energy.

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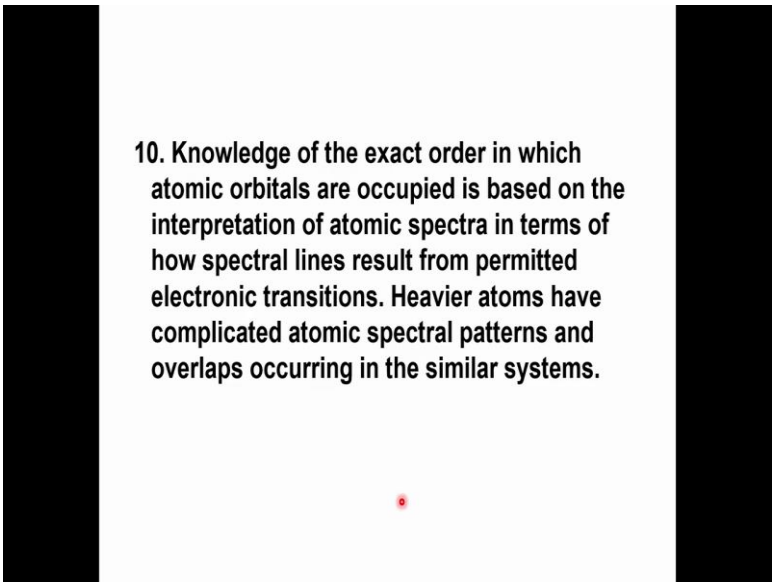

So, knowledge of the exact order in which atomic orbital's are filled by the electrons is based on the interpretation of atomic spectra. We can take a look at the spectra and say how the electrons are filled in the atom that is the beauty of spectroscopy. It is based on the interpretation of atomic spectra in terms of how spectral lines result from permitted electronic transitions. So, in all atomic spectra there are transitions occurring in between the each other and then the transitions occurring can be interpreted by the spectra and knowledge of the exact we can use this knowledge to determine how electrons are organized in each element; that means, by looking at the spectra we should be able to identify the element that is the basis of spectroscopy you understand.

So, this is what you are looking at in the atomic absorption spectrometry also that is why I am giving you so much in detail about the atomic spectra, but once these fundamental things are identified we will not have any confusion later when we go into instrumentation and other aspects. Now the heavier atoms have complicated atomic spectral patterns; obviously, it is understood because there are a lot of electrons and more in atomic orbitals, more magnetic orbitals, more spin orbitals and then it overlaps system overlapping system is also there like that we can (Refer Time: 30:22) we can predict the spectrum based on the number of electrons.

Now, this is the slide I have already shown you that the electrons are a electronic arrangement we will not go into details.

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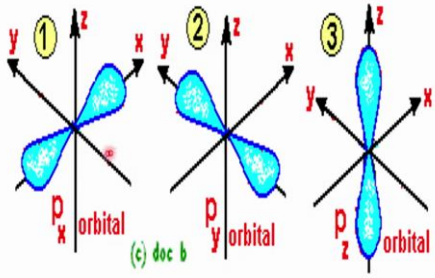

But they can just to stretch your imagination I want to show you this is a 3 D picture this is a 2 D picture in a planar structure, this is also a planar structure this is a 3 D picture in the space. Now you can also imagine that the d orbital's p x, p y etcetera they are organized like this there are (Refer Time: 31:05) there has to be 3 p orbital one will be along x axis, one will be alone the y axis and other will be perpendicular. So, p x we call this p x, we call this p y, and we call this p z. So, 3 orbital's there is not much interaction between these 3 electro orbital's; that means, electronic transitions do not occur in all the 3 orbital's because they do not overlap in any way with each other. You have to imagine a 3 D structure and draw a figure then it will be easy for you to imagine how these orbital's are organized.

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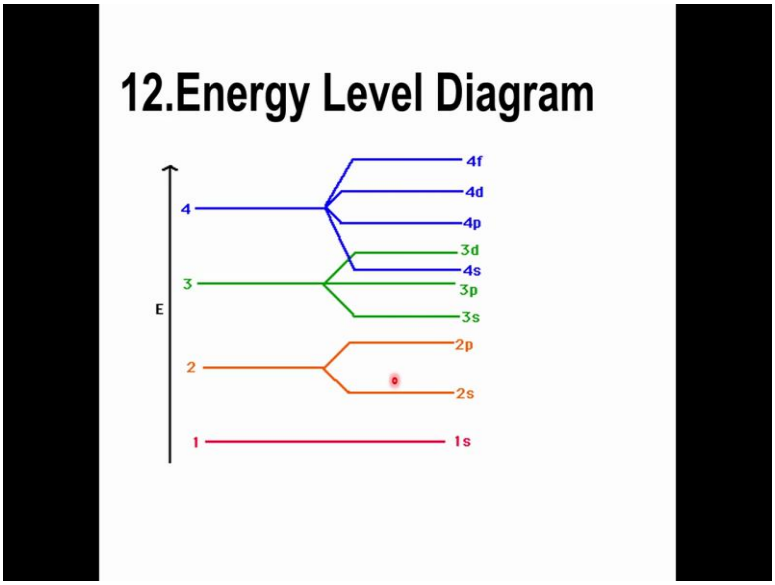

Now, I can depict the same in terms of energy. So, here you can see 1 2 3 refers to principal quantum number, and this is the potential energy and then in principal quantum number n I have only one orbital that is 1 s, in here it is 2 2 s 2 p, and then in the third one there is 3 s 3 p 3 d and in number quantum number 4 I have 4 s, 4 p, 4 d, 4 f, but you can imagine that the 4 s is lower in energy than 3 d, this is what I was talking about overlapping of the energy levels.

So, if you remember this structure you can keep on feeling 2 2electrons in each orbital of course, the here 2 p refers to 2 p x, 2 p y, 2 p z which are equivalent say similarly it is 3 p x, p y, p z and 3 d means other 4 electro 4 orbitals in the space like that; now if you remember this you will be able to fill all the electrons corresponding to all the elements in the periodic table.

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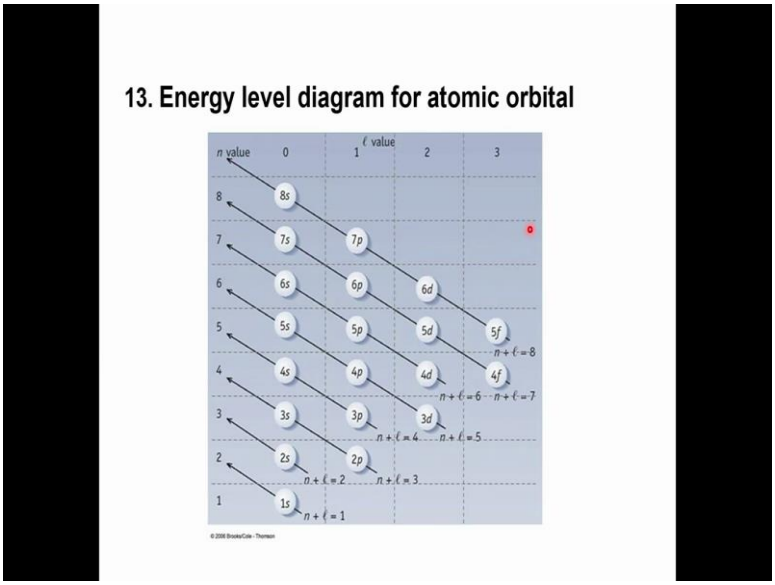

Now, this is how it goes, this is energy level diagram for the atomic orbital that is I have here 1 1 s principal quantum number n and then l that is equal to 1, and then here it is 2 energy level and value and then this is the different energy levels 1 s, 2 s, 2 p, 3 s, 3 p, 3 d like that we will be able to see the diagram. So, this is a very famous picture how the electrons need to be filled if I give you an numbers atomic structure you should be able to fill the electrons corresponding to each orbital in a given system.

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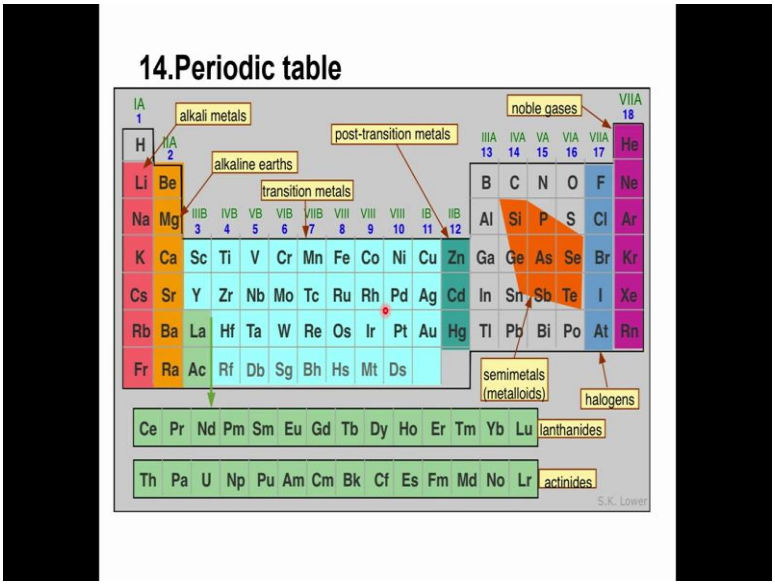

Now, this is how we do for example, hydrogen has got one electron. So, the one electron that is there is 1 s then next element is helium. So, helium has got 2 electrons. So, it can be 2 s here, similarly it is 1 s 2 a lithium will be 3 electrons. So, this will be 2 and there will be 1 electron in this, then lithium beryllium beryline will be having one more. So, it will be having 1 electron in 2 p, 2 p x then the next element hydrogen, helium, lithium, beryllium, boron; boron will have 2 p x, 2 p y and next element will be having 1 in 2 p z also after that 3 more electrons can be filled in 2 p x, 2 p y, 2 p z like that you can keep on feeling all the orbitals with 2 2 electrons corresponding to s is equal to half, and s is equal to minus half.

So, this is the periodic table what we normally have in all our textbooks it is hydrogen, helium, lithium, beryllium, boron, carbon etcetera here these are all d orbital the electrons will go inner shells, this is known as the alkali metals these are alkaline earth metals, these are transition metals, these are this is post transition metals, zinc, cadmium and mercury and we have the main this thing silicon, phosphorus and germanium these are metalloids, these are all metals and then we have halogens here, fluoride, chloride bromide and iodide and astatane and then we have the neutral elements that is helium, neon, argon, krypton, xenon and radon, these are all semi metalloids, halogens and lanthanum series I have here from lanthanum to lutetium these are known as lanthanide elements these are this elements will have electrons filling in the f orbitals. Same thing is true with actinides that is starting from actinium up to this nubium and lawrencium it is known as 5 f orbitals. So, this is how the periodic table looks and the electronic arrangement can be guessed or can be predicted or can be allotted and this is our familiar picture.

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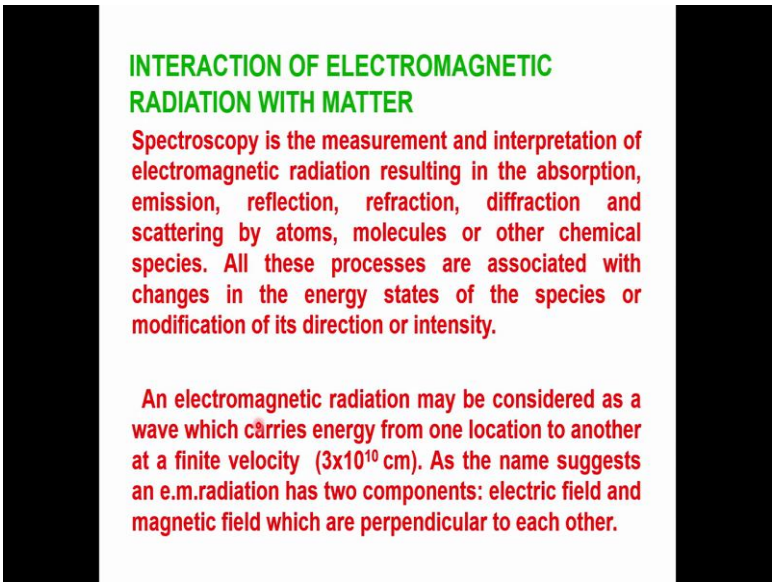

So, now what do you want to do is will explore the interaction of electromagnetic radiation with matter normally if we know the electronic structure of an atom and then to generate a spectrum it has to interact with the electromagnetic radiation. So, the electromagnetic radiation how does it affect the structure of an atom, when it impinges upon a metal. So, this area of study is known as spectroscopy; now in spectroscopy what we are looking at is the radiation falling on matter can undergo several changes and you can imagine that some of the radiation maybe if you take a mirror allow radiation to fall it you will see the image at some other angle.

If you look at yourself you will see your image perpendicular to it and part of it may be emitted part of it may pass through if you hold a small paper in front of a flame you can see that the paper also we will look a little reddish on the other side; that means, part of the radiation is coming out of the paper try this experiment at home, take a small paper who hold it in front of a flame you can see part of the radiation coming out it is a very simple experiment everybody must have experienced such things and then if you look at it may be reflected and you can see the reflection of yourself, and material it can be refracted, it can be diffracted, it can be scattered it can be material can be scattered the image can be scatter. So, atoms molecules and other chemical species also behave the same way if they are exposed to the metals if a electromagnetic radiation; that means, metal atoms containing nucleus and electrons if exposed to electromagnetic radiation can

cause electromagnetic radiation to defuse, to reflect, to diffract and then to scatter it so many things can happen to the radiation not to be metal.

So, all these processes are associated which changes in the energy states of the species or modifications of its direction and intensity anything can happen. So, we will be study these changes in our next class.