Infrared Spectroscopy for Pollution Monitoring

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Lecture-06
Atomic Structure III

We will start of where we left in the last session that is regarding the hydrogen spectrum and I had showed you this slide when the showing that.

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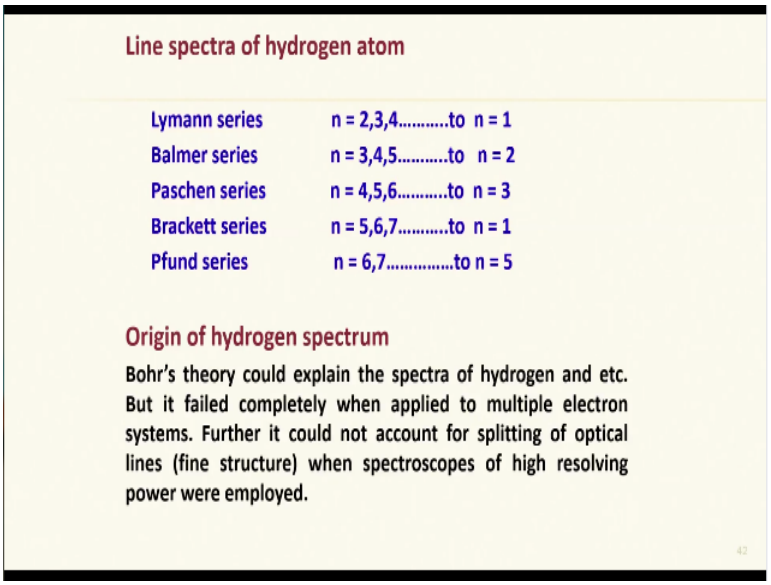

The Bohr's theory it could not explain the hydrogen spectrum in all it is entirety but also when apply to multiple electronic systems with was it failed to occur for all the line spectra's.

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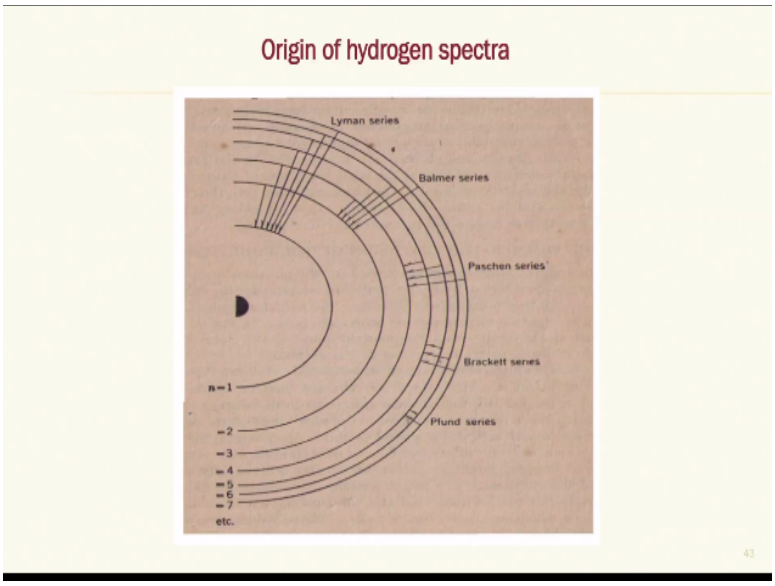

So, this is the origin of line spectra what we are talking about and you can see this is n=1 and electrons from here and here n=2, n=3, 4, 5, 6, 7 are there. And one of them when they fall to this range n=1 this Lyman spec series, this is known as Balmer series and Paschen series n=3, Brackett series and Pfund series. So the area of spectrum visible region and other spectrum they are all different for n=1.

So all the things that are visible in indeed ultraviolet region are n=1, in all the things that are visible in the n=2 they are all in the visible region. And like that these are near IR etc. the beauty is people first noticed only this Balmer series for the first time. And later on they discover these serial Lyman series, Paschen series etc. as the understanding of the spectroscopy improve to higher level.

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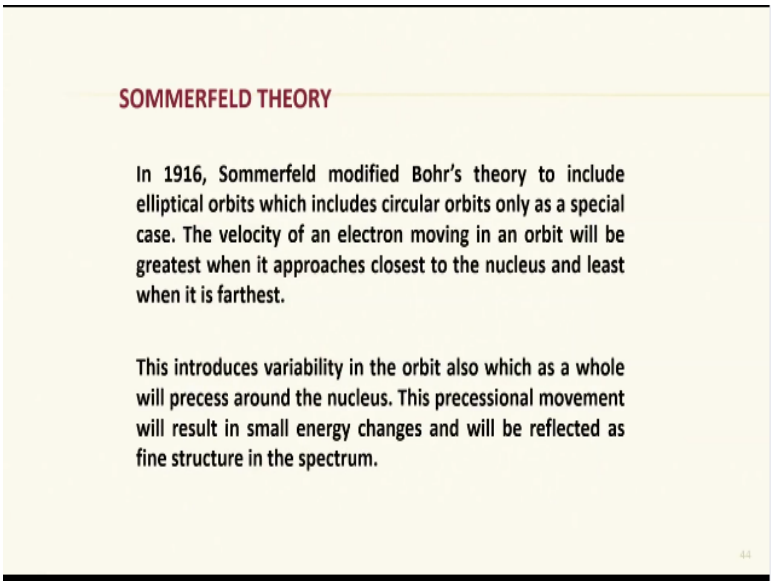

So, in the Sommerfeld theory there was slight improvement over the Balmer's theory that he modifies Sommerfeld's theory to include elliptical orbits instead of the circular orbits, see this slide we have shown all the orbits as circular orbits. This is a nucleus, these are the electrons, stationary orbits where electrons are populated and these are all circular, Sommerfeld modified them into sort of elliptical orbits instead of circular orbits.

So what it means essentially is that the velocity of an electron moving in an orbit will be greatest when it approaches closest to the nucleus and least when it is farthest. So this was the improvement over Bohr's theory, that also Bohr's theory was somewhere around 1903 or 1912 or something. But the subsequently 1916 is fairly longtime in the chronology for development of science.

But anyway came in 1916 and the analogy exist that with planets where they also are supposed to undergo elliptical have an elliptical orbit. And when they are nearer the sun their speed of revolution increases, a speed of movement increases when they are nearest to the sun and reduces considerably when they are away from them. It all depends upon the major and minor axis of the elliptical orbits.

So the variation in elliptical orbit as a whole has an idea that the nucleus precesses around itself. So electrons also must be precessing around themselves just like our planet earth is going round

and round the sun but it is also going round and round itself. So, this precissional movement will result in small energy changes and will be reflected as fine structure in the spectrum.

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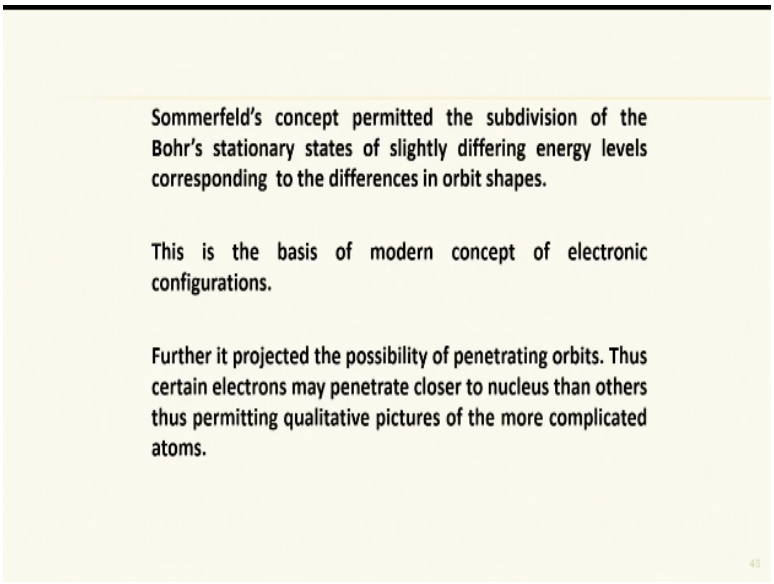

So, Sommerfeld's concept permit at the subdivision of Bohr's stationary phases of slightly differing energy levels and corresponding to the difference in the orbit shapes, orbital shapes. So, this is the basis of our current modern concept of electronic configurations. Further it projected the possibility of penetrating orbits, see the so long as the electrons are moving in an empty space and n=1, n=2 there could be elliptical orbits.

And then elliptical orbit 1, elliptical orbit 2 etc., there could be some sort of penetration because it is all empty space okay. The path to be described is only in the space, so it permitted the possibility of penetrating orbits for different quantum numbers. So certain electrons may penetrate closer to the nucleus than others. So thus permitting 1 qualitative pictures of the more complicated atoms.

So, now a days if you take a look at the electronic structure of the atoms in the Google or something like that you will see that highly confusing structure of the electrons where it could be around the nucleus etc.. I suggest you take a look at such pictures in your mobile or in your computer if you have you will see that they are fairly complex structures which penetrate each other also orbits okay.

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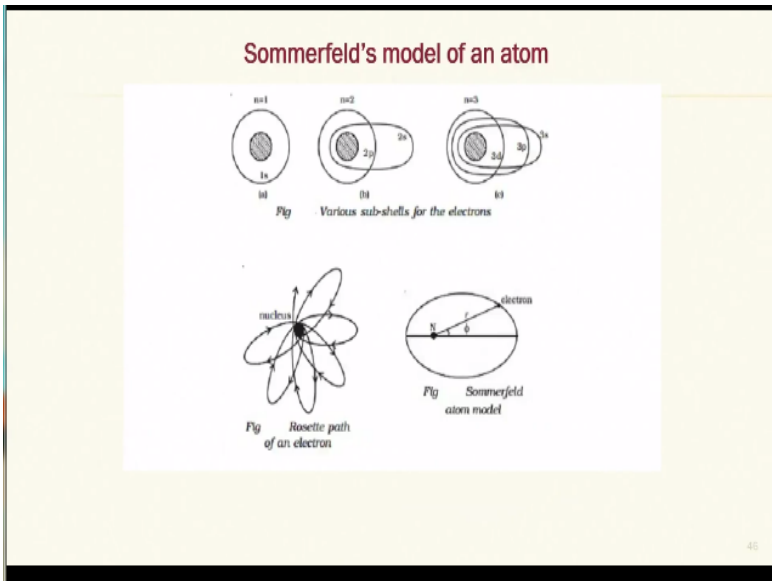

So, this is the how the orbits penetrate in the electronic structure, we can see here in the figure the 1s is here and then there is one more here. And this is 1s and then 2, 2s, 2p like that and then 3s, 3p, 3d, 2s is here and then 1 is here. So, there is penetration here already, the movement you have the second orbit into 2p, 2px, 2py. Now we will see what is 2p, 2py it is a 2pxpy etc. later.

But now I am still talking about 2p, 2d here it is 1s, 2s, 3s and then 3p, 3d and 3s, 3p, 3d bigger orbitals. And these are known as sub-shells, this was the contribution of the Sommerfeld theory and subsequently this is the Roscette path of an electron that is also very interesting how the electrons can move around in the space. This is a sort of a 3D picture actually and then the Sommerfeld's atomic model obviously it has to describe an axial path.

And another one is both axis, both are axial paths only but there could be a movement of the distance to be travel here for the same angle could be different for the distance to be travelled here for the same angle okay. So you can imagine it is a just a mathematical concept which is very clear by itself it need not to explain further okay.

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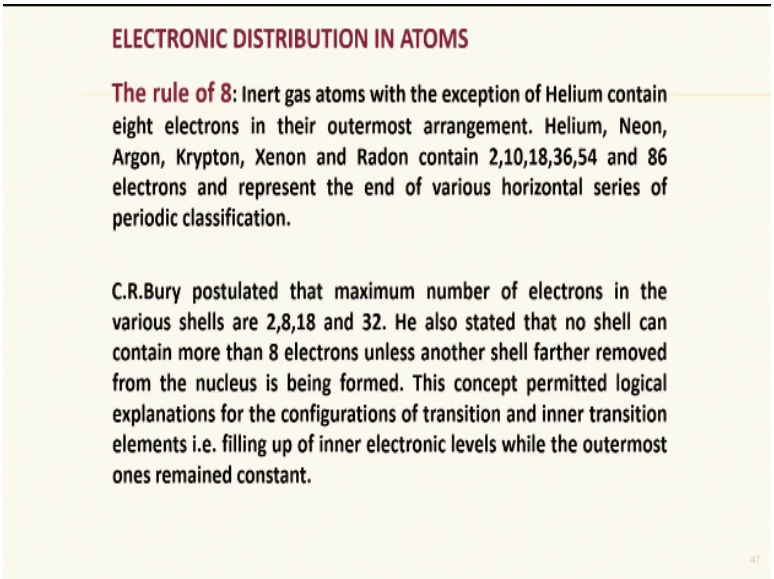

So, now we come to the topic of electronic distribution in the atoms, so there are we know that there are number of electrons as we go up the periodic table as it is. We know about 108 elements and most of them we know that even though I have taught you what is periodic table, you have most few know that there is a something called as periodic table with increasing atomic weight or atomic number.

And with increasing either property, the number of electrons by in each element increases by 1 unit. And these electrons must be arranged around the nucleus in different orbits and there are certain rules which have been in practice or which have been observed and those rules will interpret a little bit for our understanding. So these rules actually represent how the electrons are organized around the nucleus in a given space.

So look at this slide now the electronic distribution in atoms the first rule we have to consider is rule of 8. That is inert gas atoms with the exception of Helium contain 8 electrons in their outermost arrangement. So Helium has got only 2 electrons that is by nature but after Helium next element to have 8 electrons is in the outermost orbit is Neon and then comes Argon, then comes Krypton, Xenon, Radon etc.

They all these things have got 8 electrons in their outermost orbit that is total electrons would 2, 10, 18, 36, 54 and 86. So these things represent the end of various horizontal series of the

elements in the periodic table, so that means the nucleus the most of these elements are neutral elements. That means they are very stable elements not so reactive, so whenever there is a multiple of 8 there are a rule of 8 is applied.

That means when any electronic structure of an element or an ion or an atom or is a free radical something if it gains a structure similar to this with respect to the electrons present around it. If the total number works out to this range it becomes neutral. So it represents the end of various horizontal series in the periodic table as far as neutral element is concern. If the element is not neutral an element with atomic number 11 maybe if I remove 1 electron it will have a 10 electrons again it comes to neutral level rule of 8.

That means it becomes not so reactive, so an element with atomic number 12 if I remove 2 electrons it becomes 10 again it becomes very stable like that 21 remove 3 electrons it comes to 18 like that. There are number of possibilities many elements which are not just these elements Helium, Neon, Argon, Krypton, Xenon and Radon also may become non-reactive or very stable whenever certain number of electrons are removed to obtain the rule of 8 application.

So another possibility is postulated was by C.R. Bury his name is Dr. C.R. Bury he postulated that the maximum number of electrons in various shells. That is in the around the nucleus could be maximum 2, 8, 18 and 32 more than that you cannot tell. So, that is these are all based rules based on observations okay. So, he also stated that no shell can contain more than 8 electrons unless another shell further removed the nucleus is being formed.

So this concept permitted logical explanations for the configurations of the transition and inner transition elements. So very important concept this one because the electronic structure of transition elements it is wholly based on the introduction of an electron in an inner orbit without disturbing the outer orbit structure, outer electronic orbit. So, transition elements, lanthanides and actinides all the 3 series of elements there are 3 transition elements.

If you look at the periodic table, if you are familiar well and good if you are not familiar sometime later I will explain I will show you those things in a typical structure of periodic table.

But for the time being it is important for us to understand that the electrons can enter an inner orbital as the atomic weight keeps on increasing without disturbing the outer structure okay. This is the importance of Bury's postulate that maximum number of electrons in various shells could be 2, 8, 18 and 32. So suppose I have an element with 2, 8, 1 and 32 okay.

There are possibility that 17 electrons need can be added up to the third one okay. Because it has got only one instead of 18, so the next electron may got to 17 to fill up that orbit. So that is transition elements etc. etc. So, this process completed or permitted logical explanation for the configuration of the transition and inner transition elements that is filling up of inner electronic levels while the outermost orbits remain constant, they do not remain disturbed.

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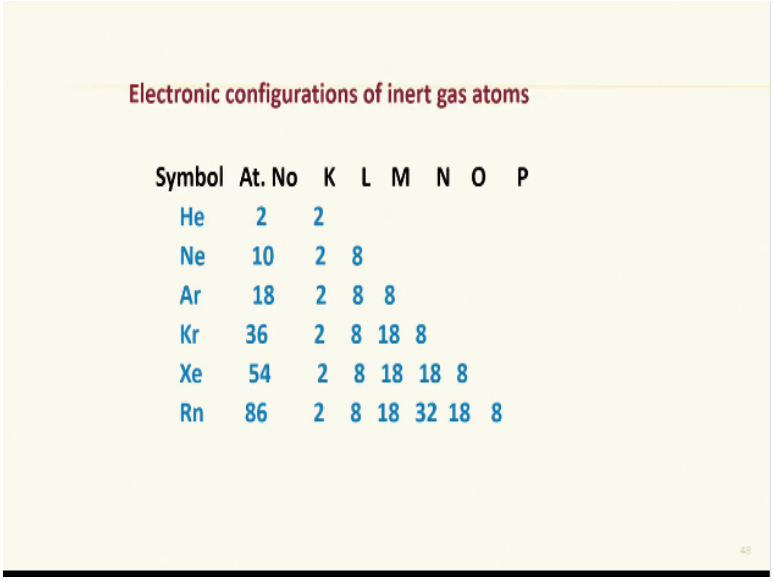

So, the electronic orbit configuration based on these 2 rules, one is the rule of 8 another is rule of 2, 8, 18 and 32, if I apply these 2 number of elements having atomic weights. You can see that the symbol here I had drawn the symbol you know Helium, the atomic number is 2, so the K shell can have only 2 electrons. And when you go to the next one atomic number is 10 but that 10 can be divided into 2 parts one is 2 and 8 that is Bury's rule.

Now Argon has got 18 and it can go up to 2, 8 and 8 maximum. So, here I have M shell, so M shell total will have 1K and L and 1 M shell total is 18, but it has got 3 orbits. Similarly Krypton has got 2, 8, 18 and 8, Xenon is 54 that is 2, 8, 18, and 8 and Radon with an atomic number of 86

is 2, 8, 18, 32, 18 and 8. Now you can imagine that there cannot be the next element with another 32 or something like that because we have already reached the end of the periodic table with 86 itself okay.

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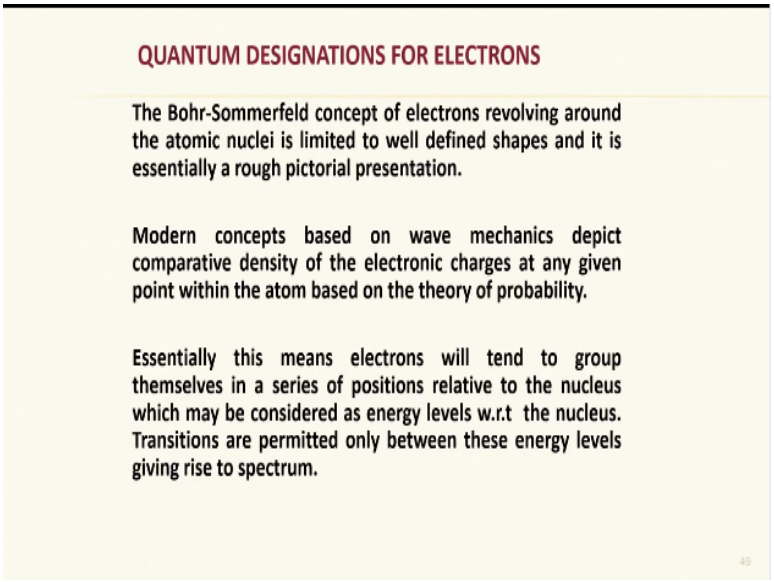

So, the quantum designations for electrons are also important and Bohr Sommerfeld concept of electrons revolving around the atomic nuclei is limited to well define shapes and it is essentially a rough pictorial presentation. Basically what we are trying to say is that the concept of electrons going round and round, I have shown you circular figure, electrical figure and many other figures.

So, even those orbiters orbits and orbital paths are only a rough pictorial presentation of the actual electron being at their around the nucleus at a particular space and time. That is the essence of quantum mechanics okay you cannot predict the position and momentum of a particle at any time exactly. There is always certain amount of error by the time you predict the position momentum changes, momentum you predict there is the position changes.

And that minimum approximation is approximately about h/2Pi or something like that but then essentially that means the electrons will tend to group themselves in a series of positions relative to the nucleus which may be considered as energy levels yes. But those energy levels are with

respect to the nucleus. So, transitions are permitted only between these energy levels which are present around the nucleus and the energy levels are also not exactly defined.

But they are all our imagination that if an electron is at such a particular height or distance from the nucleus. It is energy level could be this much if it is more it is energy level could be this much like that but they are not exactly defined you know you cannot see them in actual figure. So these energy levels how do we infer them in by spectrum that is the beauty of spectrum and every electron in an element can be described in terms of it is quantum numbers.

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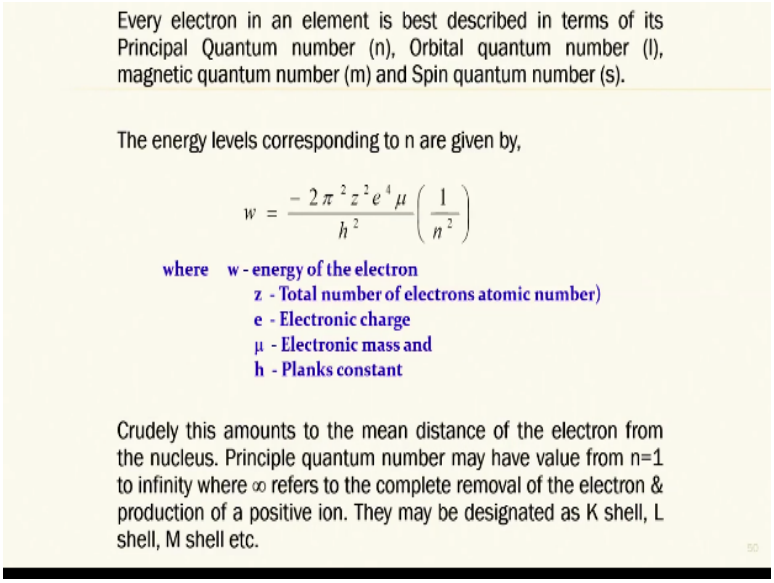

One is principle quantum number n, another is orbital quantum number l, third is magnetic quantum number m and fourth is the spin quantum number s. So, n, l, m and s are the 4 quantum numbers and the energy levels corresponding to the orbit n would be something like this W=-2 Pi square, z square, e to the power of 4*mew divided by h square multiplied by 1 over n square. So, this term is not very important as far as your course is concerned or exam is concerned.

But it is good to understand these things here in this equation w is the energy of the electron and z is the total number of electrons, that is atomic number and e is the electronic charge the e raise to 4 is here. And mew is the electronic mass that is here okay and h is planks constant that is here. So, z is the total number of electrons that is atomic number, so crudely this amounts to the

mean distance of the electron from the nucleus which one is w=-2 Pi square z square e to the power of 4 mew*1/n square/h square.

So the principle quantum number I can have n=1, n=2 etc. up to n=infinity but infinity means it is not there okay the electron must have escaped. So, infinity refers to the complete removal of the electron from the influence sphere of the nucleus that means it produces a positive ion and they maybe desire the paths described by the time they starts from the lowest end of the level to next highest energy level until it reaches the escape level.

They can be designated as K shell, L shell, M shell etc., so the now we will describe what is l, earlier I had described n=1 to infinity. Now in the previous equation we are not written l.

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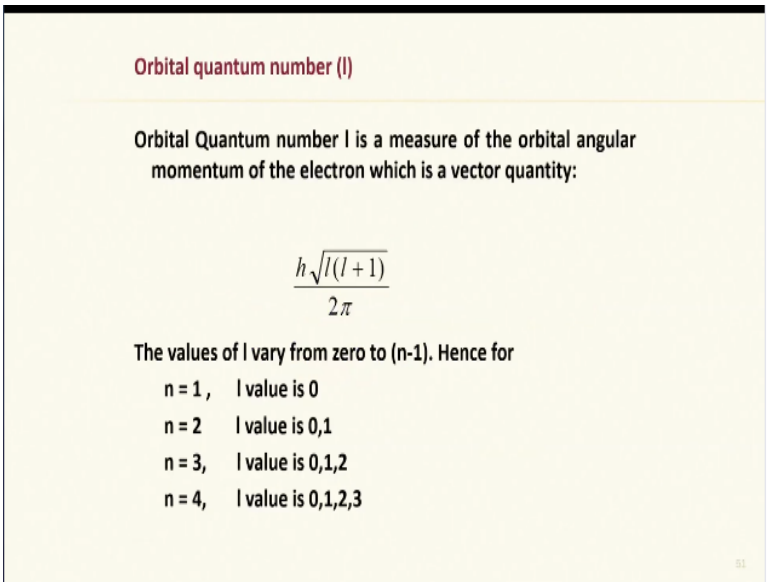

But the second quantum number that orbital quantum number l is another address for an electron that is any electron can be given some numbers corresponding to n, l, m and s okay. So, the orbital quantum number l is a mixture measure of the orbital angular momentum of the electron which is a vector quantity. So, what is the vector quantity, find out okay, I may ask you in the exam, so better find out what is the vector quantity.

So, if l is a orbital quantum number that is h*square root of l*l+1 divided by 2 Pi and the values of i the values of l may vary from 0 to n-1. That is if n=2 l could be equal to 2-1 that is 1, n=1

means l should be 0, that is the energy of the material or the electron corresponding to n=1. So, when n=2 the value of l would be 0 and 1, so n=3 it goes to 0, 1 and 2, l=4 it goes to 0, 1, 2, 3 etc. etc.

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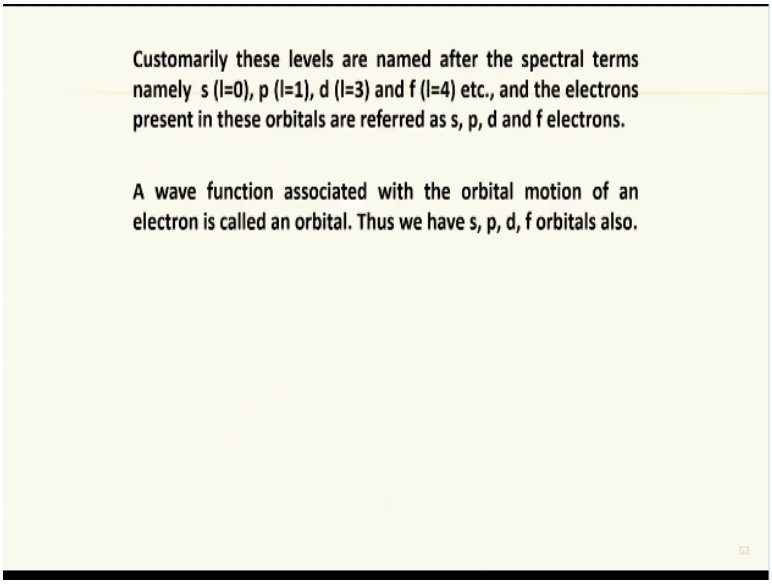

So, customarily these levels are named after this spectral terms that are obtained in the spectrum and in the spectrum we define the spectral terms as s, p, d and f okay. So, they are the jargons of spectroscopists. The spectroscope is described it is s, s means l=0 orbital angular momentum and p is means l=1, d is l= 3, f is while=4 etc., and the electrons present in these orbits are refer to as s, p, d, f electrons okay.

Now a wave function these associated with orbital motion of an electron that is called as orbital, the electron being very small it will not be moving like a cannon ball or a pistol ball but it will be moving like a wave. And yesterday I had told you that the movement of a wave can be described by what is the height of the wave, what is the distance of the wave, what is the number of cycles or how many cycles are completed per minute or something that is frequency.

So the wave function of an electron which is in orbital motion of an electron is called as an orbital. So we have s, p, d, f orbitals also. So, what we have now whenever we are trying to describe the electrons atomic structure we say s, p, d, f electrons are there s electrons, p electrons, d electrons and f electrons but we also say there is s orbital, p orbital, d orbital and f

orbital also. So s electrons are there in s orbital but still the electrons are also referred to as s, p, d, f and orbitals are also refer to as s, p, d, f orbital just to distinguish them from each other okay.

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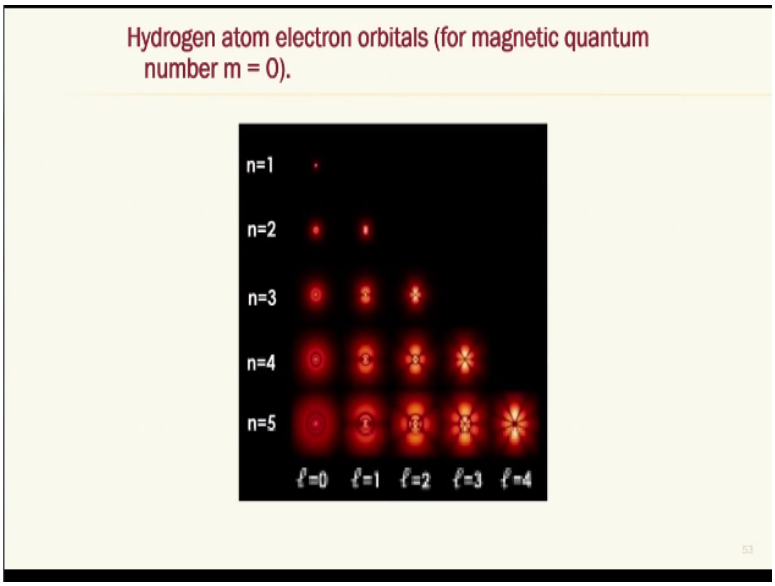

Now here is a picture of the hydrogen atom electron orbitals okay, for magnetic quantum number m=0. So, here again we have shown n=0 means n= here the see only one orbit n=2 means 2 are there, n=3 it is like this, n=4 you can make out n=5. But here in this case in all these cases l=1 here right from n=1 here it is n=l=0, why because n=1, l should be n-1, so this orbit is defined as l=0.

Similarly if n=2, l should be 1 and there is no possibility for his to be l=2 therefore I have the orbital when l=1 I have an orbital arising from n=2 orbital arising from n=3, orbital arising from n=4 and orbitals arising from n=5. Similarly when n=2, l=3, l=4 all these thing possibilities are there with respect to the electronic orbitals.

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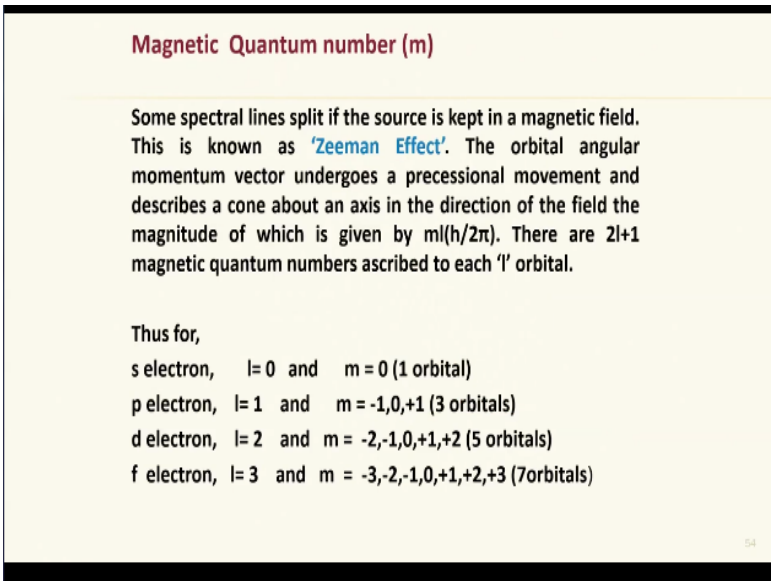

So, the magnetic quantum number now we are going to define it is not easily visible in our day today life of a spectroscopist or a physicist who wants to look at the electronic structure. But only when you put a magnetic field around an electron then you will see some effect in this spectrum not around the field okay. So, what is the effect, the spectral line which is 1 single line will appear 2 instead of 1 it appears 2 okay.

So, 1 single spectral line appears like this there could be parallel not necessarily originating from the same point. They are they will appear as 2 parallel lines in the whenever a magnetic field is applied, so this effect is known as Zeeman Effect. The very important concept in atomic absorption as well as in many systems where I was I have taught earlier and especially atomic absorption and ICP inductive couple plasma.

So, this is known as Zeeman Effect the orbital angular momentum vector it undergoes a precessional movement that describes a cone okay. Now look at it like this the orbital angular electron is here the moment I put an electron you can see here I have turning a little bit. So, it will start moving around, so the processional movement of the electron described a cone, the cone means you know what is it cone, cone means it is a cylindrical thing from the bottom a it is like a small packet of paper packet what you get in ice-cream okay, Ice-cream cone you are all familiar.

So, you can imagine and ice-cream cone sharp at the bottom open at the top but it is going round and round in that space. So, it describes a cone about an axis in the direction of the field and the magnitude is given by m, l*h/2 Pi. That means the area of the cone on the top where maximum area is there that is given by ml*h/2 Pi, so it keeps on going like this. So, there are 2l+1 magnetic numbers ascribed to each l orbital.

So, for electron s, s electron there l is 0 and m=0 before y because 2l+1, 2*0+1 is 1 only isn't it. So, there is only one orbital but the corresponding magnetic quantum number is 0. So, for 3 electron l=1 and 2l+1 means there will be -1, 0 and +1 and why -1 means it is only a positional effect. So, with respect to particular measurement axis, so if it is below -1 if it is above +1 and if it is on the same place it is 0.

So, I have -1, 0 and +1 and for ready electron I have l=2 and that means 5 orbitals are there -2, -1, 0, +1 and +2 and f electron also is there that is l=3 it is it has got about 7 orbitals. So we will describe about the spin orbital the spin quantum number in our next class which has something to do with the electronic spin.

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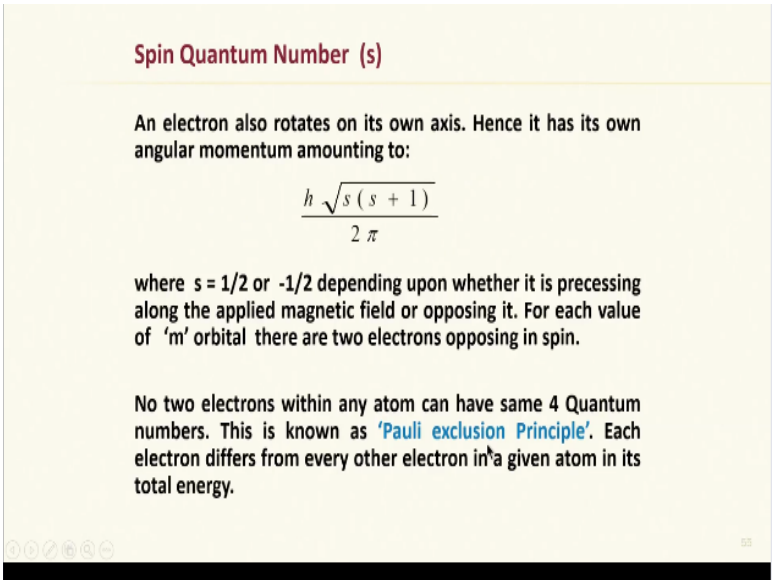

So, what do have described so far is how an electron in a given system can be defined individually every individual electron can be defined by 4 quantum numbers, 1 is n, 1 is l, 1 is m, 1 is s, we have understood what is n principle quantum number l is angular quantum number, m

is magnetic quantum number which is visible only on the application of magnetic field. We will continue our discussion with respect to spin quantum number and complete our understanding of the electrons in the next class, thank you very much.