Atomic and Molecular Absorption Spectrometry for Pollution Monitoring Dr. J R Mudakavi Department of Chemical Engineering Indian Institute of Science, Bangalore

# Lecture – 04 Atomic and molecular orbitals

We have been discussing about the electron my interaction of electromagnetic radiation with matter, now I hope that you are understanding what is electromagnetic radiation.

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(Refer Slide Time: 00:40)

So, I am presenting in front of you this figure of the electromagnetic spectrum. So, I told you that the electromagnetic radiation that we come across in our day to day life is a bundle of energy containing different frequencies. Now in this figure I have here on the top left on the left side have put the way wavelengths, it starts from 10 raise to minus 6 nanometer, and 10 raise to minus 5, minus 4, minus 3 like that for I have listed them out and then up to 10 raise to minus 1 nanometer it is here. 1 nanometer is 10 raise to minus 6 meters, so after that I have listed started from 1, 10, 100, 100 10 raise to 3 nanometer 10 micrometer etcetera here the scale changes we do not call it nanometer anymore, but all are interconvertible.

So, on the left side I have 10 micrometers now, 10, 100 and 1000 and then after that we are talking moving into millimeter range that is 10 mm, 10 centimeters, 100 centimeters

and then afterwards moving down still down I have 10, 100 and 1000 meters that is a then I have upto 10 kilometer, 100 kilometer and then 1 million meters, 10 mm and 100 meters. So, in the middle I have gamma rays that is gamma rays range from 10 raise to minus 6 to 10 raise to minus 2 nanometers. The top 5 corresponds to gamma rays; below that I have x rays the wavelength range will be from 10 raise to minus 1 to 10 nanometers. So, part of the electromagnetic radiation is also composed of x rays.

And lower side I have ultraviolet rays and I am still you go down you come across visible range which is a very small portion of the total electromagnetic radiation spectrum, then after the visible range I have near infrared, far infrared, and then microwave. So, microwave you are all very familiar with ranging from 1000 micrometer to 1 meter. 100 centimeters we use microwave in our day kitchen also ovens based on microwaves are available, and then radio waves of course, you would be familiar because that is where you will be hearing lot of music and other things they all contain they all range from 100 centimeter to 100 millimeter megamergers.

So, the whole electromagnetic radiation can be classified as gamma rays, x rays, ultraviolet rays visible light near infrared, far infrared, microwave and radio waves. So, yesterday I have explain to you that gamma rays are all products of nuclear reactions and they are nothing, but basically neutrons, which are being emitted and x rays are when electrons bombard on metals x rays are produced, and these are having slightly higher wavelength range then gamma rays. Ultra violet range are still weaker in terms of energy and longer in terms of wavelength.

So, next comes visible the ultraviolet rays are all part of our suns energy which is supposed to contain vitamin d also, and then visible light it visible light has a several components violet, indigo, blue, green, yellow, orange and red and next to that we have near infrared far infrared, infrared lamps people use in day today life for the operation of for sports persons whenever they get injured infrared lamp is focused on the four parts affected by the body bruises etcetera it is used as a painkiller.

So, we are all very familiar with most of these radiations except gamma rays maybe in a you may not come across day to day life, but x rays medicine ultraviolet is used in this sunscreen lotions and things like that visible light of course, I do not have to explain to you, everywhere you see all around you visible light near infrared; near infrared and

infrared, far infrared are used for sports persons treatment and microwaves are used for we used in the kitchens, radio waves for music and entertainment etcetera. And then again a microwaves and radio waves are classified as uhf vhf and hf etcetera ultra high frequency very high frequency high frequency like that and very low frequency and below that we have audio this thing. So, you can see that the electromagnetic radiation the visible light what we are now what we normally are exposed as human beings it forms a very small portions of very small portion of the total infrared total electromagnetic radiation. And for our spectrophotometer for this course will be concentrating on ultraviolet and visible light, and near infrared light also radiation also to some extent.

(Refer Slide Time: 07:21)



So, this is what you have been talking about, we will continue our discussion basically how our knowledge of to determine how our knowledge of spectroscopy has developed over a period of time.

### (Refer Slide Time: 07:31)



So, basically all can be traced to electronic structure of the atoms, and I have already explain to you that Sir J.J Thomson's work about electrons and neutrons etcetera Rutherford's modified theory also we had looked at it, and our next understanding of the spectroscopic techniques came from Bohr and Niel's pressure Niels Bohr a Nobel (Refer Time: 08:04) who proposed radically different view of the atomic structure based on the optical spectrum of hydrogen. He included the postulates of quantum theory by max Planck also. So, what essentially Bohr reported is that the electron in a hydrogen atom is always describes a fixed circular around the nucleus; that means, electron is going around and round the nucleus that is the Bohr model. So, such orbits are there named as stationary orbit.

Actually what I want is I want you to understand that there is a nucleus like this electron is going around, when the electron is excited to next higher energy level its diameter would increase and it will be going at a still higher energy level. Again if you increase provide more energy again it will described a bigger path, but still going around and round the nucleus, you supply lot of energy it may electron may go off; that means, it will ionize. So, the orbits in which the electrons are moving around the nucleus are known as stationary states in Bohr Theory, and he thought of various circles referring in radius. The angular momentum of each stationary states was an integral multiple of n h by 2 pi, that is planks theory what he said is in quantum mechanical theory when you supply certain amount of energy electron goes to next higher energy state, but it has to be a definite quantity of energy corresponding to the energy difference between the final state and the lower state.

So, in between suppose you in supply energy in between the 2 states it will have no effect, it will not excite the electron to neither higher energy level nor it will fall back. So, that is Planck's theory. So, in Planck's theory the energy difference between the 2 states is given by n h by 2 pi and the angular momentum of the electron because we do not want the electron to fall back into the nucleus. So, it has to be balanced by the angular momentum which will be exiting some sort of a centripetal force to keep it in circulation. So, that angular momentum is given by mvr is equal to n h by 2 pi where n is an integer called as quantum number. I think you are all familiar with this and he also postulated that as long as the electron remains in a given orbit it neither radiates nor absorb energy.

(Refer Slide Time: 11:00)



So, that is the fundamental truth. So, when the electron moves from one orbit to another it was considered to involve absorption or emission of energy. So, this energy manifests as radiation and the frequency of such radiation is manifest in as a spectral line, in which could be related to the energy of the electrons in the 2 states E 1, E 2 or E final or E initial like that; what we are saying is there is a nucleus electron is going round and round I am going to supply energy and when I supply the energy electron will go to the next higher energy level, at that time a certain amount of radiation is going to be either absorbed or emitted if it falls from higher energy to level to lower energy level the difference is emitted. So, if you take the total energy of the radiation before excitation and after excitation there will be certain amount of energy difference between the 2 states right. So, this energy difference is the spectroscopy.

So, the energy difference I can put a photographic plate. So, as the electron moves from one to higher energy level if I put a photographic plate there will be certain amount of signal, corresponding to the 2 different energy states; if the electron is occupied there will be occupied signal, if it is not there if it is excited then there will be some amount of light will be emitted or excited or absorbed which can be measured. So, each transition is always accompanied by certain amount of spectroscopic evidence, which manifests itself as a sharp line on the photographic plate and in the energy level spectrum diagram also energy of the incoming radiation. So, if you take hydrogen supply certain amount of energy electron will be excited to next higher energy so there will be one signal, and then suppose you excite it to next higher energy level there will be second signal.

So, suppose there are number of electrons at the same energy level all of them going from the same energy level to next higher energy level, there will be certain amount of transitions. These transitions suppose the electron is at the ground on the first step imagine a very simple analogy is imagine the number of stairs from ground floor to third floor or fifth floor. So, first floor there will be a platform, second floor there will be another platform, third floor will be another platform. Now some electrons are at the ground floor you take a imagine a football and kick it to the first floor, that energy is difference the moment it hits the first floor you are going to get a signal. Some sometimes you may hit the second floor, so what happens? You will get the second signal for the same electron.

Suppose your hit is send it third floor, the again energy difference will be much more and third signal comes. Now that is one type of signal now imagine you are not on the ground floor, but you are on the first floor, from the first floor you can send it to second floor and third floor that energy difference also will be there. So, for a given element number of spectral signals will result if depending upon where the electrons are in before you supply the electrical electromagnetic radiation, some are on the ground floor, some

are on the first floor, some are on the second floor like that there will be a series of lines corresponding to each energy transitions these are known as the line spectrum.

So, the line spectrum of a hydrogen have been defined and the recorded since 1700 A D in different series corresponding to they have been grouped; for hydrogen it is a line spectrum is given as Lyman series.

(Refer Slide Time: 16:00)

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Lyman series	n = 2,3,4to n = 1
<b>Balmer</b> series	n = 3,4,5to n = 2
Paschen series	n = 4,5,6to n = 3
Brackett series	n = 5,6,7to n = 1
Pfund series	n = 6,7to n = 5
Origin of hydrogen Bohr's theory coul and etc. But it fa multiple electron	spectrum. d explain the spectra of hydroger iled completely when applied to systems. Further it could no

Here what happens all the electrons are in the ground floor that is n is equal to 1; from 1 is equal to one the electron may be transferred to n is equal to 2, n is equal to 3, n is equal to 4 like that. So, all the lines originating from n is equal to 1 are known is Lyman series. Now imagine some electrons are on the second floor n is equal to 2; from n is equal to 2 I can excite the electron only to 3 four 5 etcetera. So, all the electronic transitions or spectral lines originating from n is equal to 2 to different energy levels are known as Balmer series ok.

Similarly, n is equal to 3 is known as paschal series and then n is equal to 4 would be Brackett series and then n is equal to 5 would be Pfund series like that, but as you go from higher to higher energy levels from n is equal to 1 to 2 the energy level would be very high, one is to would be still higher, but 2 to 3 and 2 to 3 to 4 or 4 to 5 the energy difference between these energy levels would be much lower. So, the Bohr's theory could explain the spectra of origin how the different kinds of lines are obtained by the same element, but it failed completely when applied to multiple electron systems. So, this is the one of the greatest tragedies that it could not be applied therefore, it had to be modified by which took place down the line after some time further it could not account for the splitting of optical lines. For example, if you see the same like subjected to magnetic field instead of one single spectral line you will see 2 spectra spectral lines one without magnetic field one field one signal with magnetic field you will get 2 signal same line it splits into 2.

(Refer Slide Time: 18:46)



So, Bohr theory could not account for such changes at all, therefore, the Bohr model even though basically it was correct it could not explain all the spectrographic changes, it could not account for all the spectrographic changes that take place, it was slightly more the same concept what I have told you I had drawn it here, here you can see the this is hydrogen atom here n is equal to 1 the first circle first half circle is n is equal to 1.

Second half circle is n is equal to 2, 3, 4, 5, 6, 7 like that and all the transitions taking place from different energy levels to one are known as Lyman series. So, here the transitions occurring from different energy levels, but ending up only at n is equal to 2 is known as Balmer series. Third is Paschen that is n is equal to 3, n is equal to 4 is Brackett n is equal to 5 would be Pfund series.

## (Refer Slide Time: 19:42)



So, the same element hydrogen can show 5 different kinds of line spectra which can be accounted. So, the because of the failure of Bohr model what happened is down the line Sommerfeld modified bolts the Bohr's theory to include elliptical orbitals. Bohr's theory said it include the all the stationary states are circular, where as in Sommerfeld theory he said it could be elliptical also, but as a special case it can be circular just like in hydrogen. So, the velocity of electron moving in such an orbit would be greatest when it approaches closest to the nucleus and least when it is the farthest. This is a very simple assumption that imagine planet earth going round and round the sun, but when it is nearest to the sun the speed will be very high and when it is furthest the speed would be very slow.

So, this introduces the variability in the orbit also which has a hole will process around the nucleus, and this processional movement will result in small energy changes which will be reflected as fine structure in the spectrum; that is I explain to you that it is a magnetic field that makes it look somewhat more complicated instead of one single line it is double line.

# (Refer Slide Time: 21:01)



So, such fine structure could be explained by Sommerfeld theory. So, what he did essentially was he permitted the subdivision of the Bohr's stationary states of slightly differing energy levels corresponding to the differences in orbits and this is the basis of modern concept of electronic configuration also.

Further it projected the possibility of penetrating orbits; that means, if imagine an orbit like this in a round space and I can bring another orbit with an electrical magnetic field, but they can be overlapping each other. If I imagine the orbits are rigid then there is no overlapping they can be only come nearer each other only up to a certain extent, but if I have an overlapping orbit there could be certain amount of overlapping it could be 10 percent, 15 percent, 50 percent, 50 percent 100 percent like that the one orbit can overlap the other orbit.

So, the certain electrons may penetrate closer to nucleus than other in thus permitting qualitative pictures of the more complicated atoms.

### (Refer Slide Time: 22:39)



So, what we are essentially same is we can summarize the Sommerfield's theory also, in general inert gas atoms with the exception of helium contain 8electrons in the outermost orbit and helium neon argon are all having 2, 10, 18, 36 etcetera I am teaching you high school chemistry again they have so many number of electrons and represent the end of various horizontal series of periodic classification and then said C R Bury postulated that maximum number of electrons in a various shells are 2 n square that is 2,18; 2, 8, 32 and 32 these are the maximum number of electrons that can be in a any shell. So, no shell can contain more than electrons unless more than 8 electrons, unless another shell further removed from the nucleus is being for this concept permitted logical explanation for the configuration of the transition and inner transition elements.

What if you study periodic table you will see that the many of these penetrating orbitals etcetera will be there, and they all go to then added electron with higher increasing number of atomic increasing atomic number for the electron nuclear mass will increase, but the electron will go into an inner orbital not the outer orbital.

So, the orbit actual size of the element shrinks it does not expand with added electron. So, it is a beauty of the periodic table if you study that you will be knowing. (Refer Slide Time: 24:29)

Symbol	At.No	К	L	м	Ν	ο	1
He	2	2					
Ne	10	2	8				
Ar	18	2	8	8			
Kr	36	2	8	18	8		
Xe	54	2	8	18	18	8	
Rn	86	2	8	18	32	18	8

So, if I have to plot electronic configuration of inert atoms, the it should be like this helium, neon, argon, tripton etcetera here you can see maximum number atomic number would be 2, 10, 18, 36, 54 and 86 that is 2 N square rule, and the K shell will always had 2 L shell will have 8, M shell will have 8 the outer orbit outer electrons are always 8 accept the exception of helium, and inner could be 18, 18, 18 and 32 is. So, this is a very fundamental electronic configuration of the atoms which we all know and the quantum.

(Refer Slide Time: 25:16)



Now, having down the structure of the atom and a little bit about the periodic table what we want to say is the concept of electrons revolving around the nucleus atomic nuclei is limited to well defined shapes and it is essentially rough pictorial presentation. You must always remember that in electronic compositions in electronic representation of the orbits and orbitals etcetera there are no exact figures, they will always be certain amount of distortions and other things depending upon how mathematically correct you could be in incorporating the base basic conditions of the transitions.

So, modern test on wave mechanics depict comparative density of the electronic charges at any given point, within the atom based on the theory of probability. So, essentially what this means is that electrons will tend to group themselves in a series of positions relative to the nucleus which may be considered as energy levels. Have we, have been talking about energy levels in quite a long time, and these energy levels with respect to the nucleus the transitions are permitted only between the energy levels, which give rise to spectrum that is the beauty now.

(Refer Slide Time: 26:54)



Now what we are saying is the any transition that happens in a given molecule must give rise to spectrum, otherwise it is not permitted quantum mechanically it is not permitted, it has to be some sort of n h by 2 pi that the formula it must maintain.

So, the electrons are basically best described in terms of four quantum numbers again. So, one is principal quantum number and another is orbital quantum number, another is magnetic quantum number and forth is spin quantum number. So, there corresponding energy levels are given by this equation, I will not go into details about the derivation of these equations which are fairly well described in lot of textbooks, but it has not much relevance to what we are going to study in this MOOC course.

(Refer Slide Time: 28:00)



So, but for our practical purposes they orbital we can say that the quantum orbital quantum number is a measure of the orbital angular momentum, that is given by h into square root of l into l plus 1 divided by 2 pi; similarly I can describe the spin quantum number also and magnetic quantum number also.

### (Refer Slide Time: 28:23)



And the magnetic quantum number will be in off will come into play only if we have a magnetic field, and if this normally in magnetic field spectral line split and that is known as Zeeman effect, and this Zeeman effect is also very part of our spectroscopic techniques which are very very very important, which takes place in the atomic absorption spectrometry that we are not dealing here right now we are dealing only with the molecular spectroscopy, but Zeeman effect we should all be very familiar with respect to splitting of the spectral lines in magnetic field.

(Refer Slide Time: 29:14)

The magnetic quantum number is an integral value and varies from -I to +I. Thus for s electron s electron I=0 and  $m_1 = 0$ p electron I=1 and  $m_1 = -1, 0, +1$ d electron I=2 and  $m_1 = -2, -1, 0, +1, +2$ f electron I=3 and  $m_1 = -3, -2, -1, 0, +1, +2, +3$  So, the magnetic quantum numbers change from 0, 1 is equal to 0, 1 is equal to 1 means there will be 3 magnetic fields, minus 1 plus 0, 1 plus 1 like that. So, different magnetic splitting will take place.

(Refer Slide Time: 29:35)



And the spin quantum number spin all the electron also can change that is given by this expression h into square root of s into s plus 1 divided by 2 pi, but the spin quantum number can have only 2 values that is plus half and minus half. So, without going into details the we just have to confirm now that the in any orbital there can be only 2 electrons within any atom that has all; that means, all the four quantum numbers cannot describe single electron or 2 electrons, no 2 electrons will have identical four quantum numbers that is what it means finally, it is just like having a rupee note which is different which is similar in all aspects accept the numbers. So, similarly every electron has an address containing n 1 m and s quantum numbers.

(Refer Slide Time: 30:50)



So, knowledge of the exact order in which electrons atomic orbitals are occupied is based on the interpretation of atomic spectra only. So, our knowledge of comes only from atomic spectra in terms of how spectral lines result from the permitted electronic transitions. So, heavier atoms will have definitely more number of electrons more number of orbitals more overlapping. So, the spectrum would be more complicated than simple items like hydrogen.

(Refer Slide Time: 31:25)



So, here is a practical representation of atomic orbitals, and here s orbital you can see on the left side that is fairly spherical and the p orbitals are distributed about the bond axis and the bond there black line in between the 2 represents the x and y axis, and we can see that up p orbitals are dumbbell shaped I placed above and below along the axis there is no electronic density not much electronic density, but electronic density is spread evenly on the above and below the x axis.

Similarly, there will be number of the orbital there are 3 of 3 orbitals because one would be in along x y direction, another would be y in the perpendicular direction another could be vertical direction. So, the d orbitals are further splitting from the y orbitals for your imagination we can say that the electrons are the orbitals are something like this, and again there will be 5 different d electrons and similarly there will be number of 7 f orbitals. So, these are the colored areas represent the maximum concentration of the electrons cloud in the space represented there.

(Refer Slide Time: 33:17)



So, here you can see P x orbital is one along x direction one along y direction and one along z direction. So, there could be always 3 pi orbitals and the energy levels of D again they will be in different shapes.

(Refer Slide Time: 33:33)



But they could be represented something like this 1s, 2 s, 2 p etcetera this I have already showed you in accrued form earlier.

(Refer Slide Time: 33:54)



And the energy level diagram for atomic orbitals can also be represented something like this is also a very similar very famous pictorial presentation of the filling of electrons in a periodic table ok. (Refer Slide Time: 34:12)



Now, the periodic table as we understand as of now is a modern periodic table based on atomic number and I think you are all very familiar with this hydrogen here and helium here that is the first arrow and 2 electrons, and then lithium sodium potassium caesium etcetera these all alkali metals and then alkaline earth metals transition metals, and then coinage metal fencing cadmium and mercury, palladium, copper, nickel etcetera coinage materials and these are lanthanides cerium to lutetium or lanthanides and here I have the semi metal metalloids silicon, phosphorus, sulphur gadolinium etcetera I have (Refer Time: 35:11) fluoride chloride bromide etcetera these are all very simple familiar things for you to know.

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So, based on the previous discussion we know about periodic table, we know the interaction electrons electronics filling, we know that the electrons are all around the nucleus occupying different energy levels and we also know that the energy levels can be changed the that is the occupation of the electronic orbitals and molecular orbitals can be changed by the supply of electromagnetic radiation, and this electromagnetic radiation whenever it affects a change according to the quantum mechanical rules represents a spectral line.

So, this is what essentially we have been driving at, and we will continue our discussion on the interaction of electromagnetic radiation with the matter in the next class, that is we will discuss a little about reflection refraction etcetera and then we proceed on to the spectroscopic technique of the electromagnetic radiation, that is a spectrophotometry how it works. So, based on the electromagnetic we will also look at what are the different kinds of transitions possible in electromagnetic radiation, how we can predict where is pectoral peak can be calculated without doing the experiment. So, that forms the fundamental basis of spectrophotometry.

Thank you very much, have a nice evening.