Main Group Chemistry
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Lecture – 07
Structure and Bonding aspects

Valence Bond Theory

Welcome to MSP lecture series on the chemistry of main group elements, in my last lecture I was discussing about valence shell electron pair repulsion theory and it is utility in determining the geometry and shapes of main group compounds and there we came across an important term called steric number.

Steric number is nothing, but the number of bonded atoms plus number of lone pairs number of bonded atoms means when the central atom makes a bond with a peripheral atom essentially 2 electrons are utilized. So, that is essentially bonded pair, so steric number is nothing but the number of bonded pairs plus number of lone pairs together and also we came across steric number varying from 2 to 6 and I discussed examples in each case what you should remember while using VSEPR theory is the steric number that determines the geometry, whatever the steric number is there, so that would essentially show the right geometry.

For example when you have steric number 2 and if both are bonded pairs it is has linear geometry and with steric number 3, all our bonded pairs the geometry is trigonal planar and shape also trigonal planar and steric number 4 tetrahedral, steric number 5 trigonal bi pyramidal steric number 6 octahedral and for steric number 7 the geometries pentagonal bi pyramidal and also we came across examples having both bonded pairs and lone pairs; for example, steric number 4 having 4 bonded pairs is tetrahedral, like example methane steric number 4 with 2 bonded pair and lone pair, the example is water molecules where we have 2 OH bonds and 2 lone pairs the shape is v shaped.

So, like that we discuss it in most of the cases. So, while determine the geometry consider the steric number, while determining the shape omit the lone pairs. So, far we discussed steric number 2 to 6 and I wrote the using VSEPR theory, I wrote the structure and showed you for most of the steric numbers with a lot of examples, as we progress

with the chemistry of main group elements whenever we come across examples certainly I would go back to VSEPR theory or even Lewis dot structure and the next 1 I am going to discuss his valence bond theory as well as molecular orbital theory.

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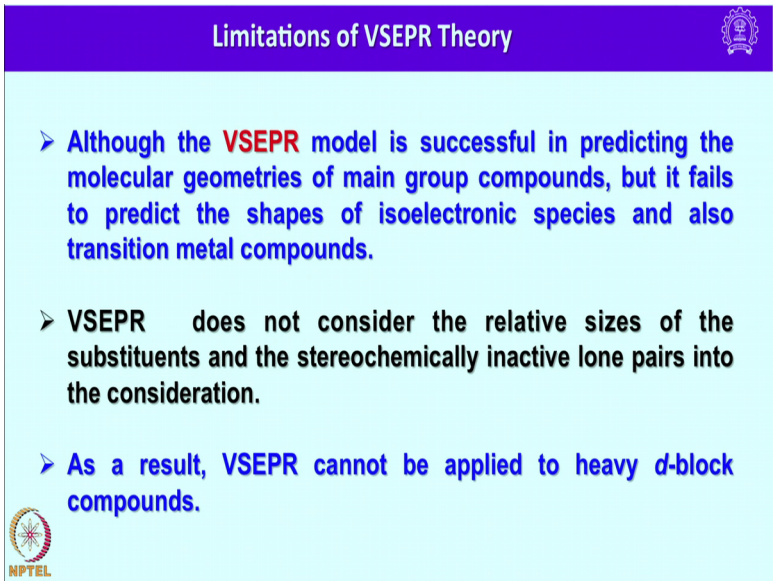

With this let me tell you something about the limitations of VSEPR theory; that means, although VSEPR theory or VSEPR model that is valence shell electron pair repulsion model is quite successful in predicting the molecular geometries of compounds and shape as well, but it fails to protect the shapes of is electronic species and also those of transfer metal compounds.

Another important limitation of VSEPR theory is it does not consider the relative sizes of the substituent and the stereo chemically inactive lone pairs that we come across often in the case of transfer metal complexes, where especially electrons in t2g are remain intact especially with pure sigma donor ligands. So, as a result, VSEPR theory cannot be applied to heavy d block compounds. So, in that context another theory came into picture that is called valence bond theory, valence bond theory uses the concept of hybridization of atomic orbital prior to the bond formation.

So, a covalent bond forms when orbital of 2 atoms overlap and the overlap region which is between the nuclei is occupied by pair of electrons in making a covalent bond. So, let us look into the theme of valence bond theory, the space generated due to the overlapping of orbital's has a maximum capacity of accommodating 2 electrons with

opposite spin; that means, when 2 orbital's are overlapping from 2 different atoms essentially, that leads the formation of a bond and that is capable of accommodating only 2 electrons of opposite spins.

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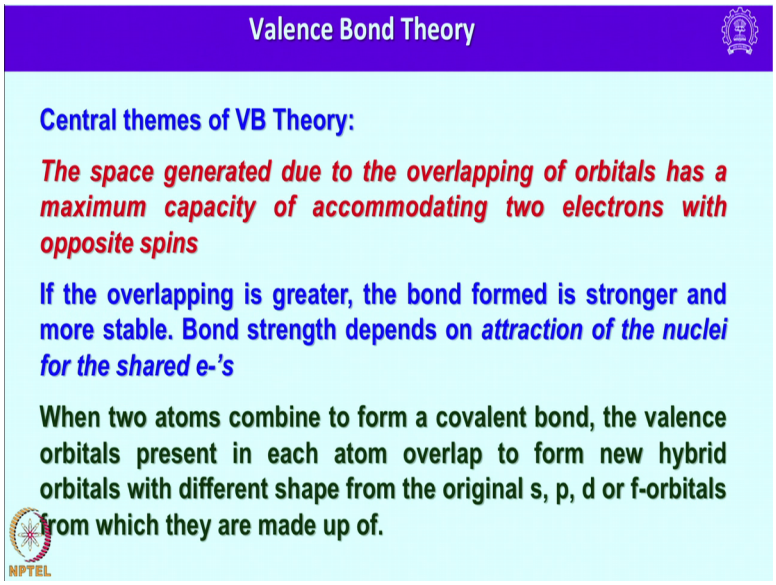

If the overlapping is greater the bond formed is stronger and more stable, but bond strength also depends on attraction of the nuclei for the shared electrons.

When 2 atoms combine to form a covalent bond, the valence orbital's present in each atom overlap to form new hybrid orbital's with the totally different shape from the original s, p, d or f orbital's, from which they are essentially made up of; that means, hybrid orbitals essentially have a different shape compared to the original orbitals from which we have constituted them. So, this hybridization concept was developed by Linus Pauling in 1931.

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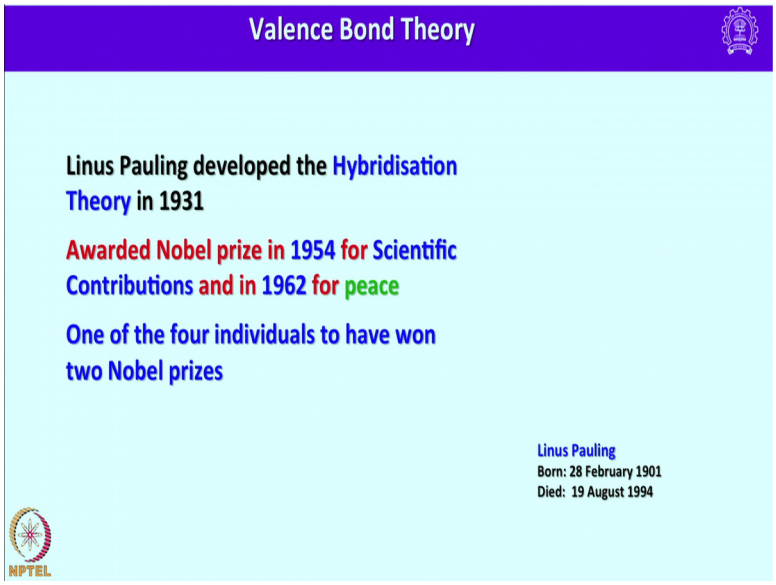

And he was awarded Nobel prize in 1954 for this scientific contribution and again he was awarded another Nobel prize in 1962 it is for it is not for chemistry, but it is for his peace activities and he is one of the 4 individuals to have won more than 1 Nobel prizes.

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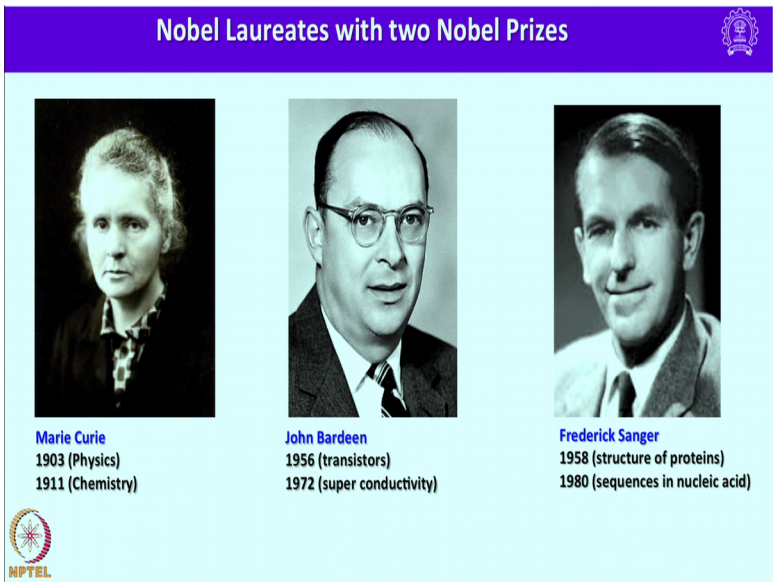

So, other 3 people are Marie curie 1 Nobel prize in 1903 for physics and again in 1911 for chemistry and then John Bardeen he won 1956 for transistors and in 1972 for super conductivity of course, he shared Nobel prize in both the instances and the fourth person who got 2 Nobel prizes is Frederick Sanger he got Nobel prize in 1958 for structure of

proteins and he shared that 1 with others and also in 1982 for sequences in nucleic acid that also he shared with others. So, as I said chemist Linus Pauling is responsible for the development of hybridization concept and he put forward his theory in 1931 in order to explain the structure of a simple molecule, such as methane using atomic orbitals of both carbon as well as hydrogen.

So, Pauling pointed out that a carbon atom forms 4 bonds by using 1s and 3 p orbitals. So, that it might be inferred that a carbon atom would have 3 bonds at right angle to each other, if you just look into a mutual orientation of px py pz, they are at orthogonal to each other. So, these 3 when combined with 3 hydrogen atoms they form angles at right angle to each other and then the fourth weaker bond is by using the s orbital of carbon with again 1 s orbital of hydrogen having position at some arbitrary direction.

However methane has 4 bonds of equivalent strength separated by a tetrahedral bond angle of 109.5. So, Pauling explained this by supposing that in the presence of 4 hydrogen atoms, the s and p orbitals from carbon would combine together to form 4 equivalent bonds each 1 having 25 percent is character and 75 percent p character and they are indicated with a term called sp 3; that means, the sp 3 indicates the composition of s and p in it in 1 is to 3, which are directed along the 4 CH bonds towards the 4 corners of a tetrahedron with having angles of 109.5 degrees.

So, this concept was essentially developed for such a simple system was later applied more widely and even today it is considered as an effective method for determining the structure and looking into the mixing of various orbital. In fact, this only gave much more input into the well defined theory that is molecular orbital theory, even in molecular orbital theory especially in case of coordination compounds when we talk about LGO Ligand group orbitals or in case of main group as well as the transfer metal complexes, we call symmetry adapted linear combination of atomic orbitals essentially we are taking hint from valence bond theory that is hybridization concept.

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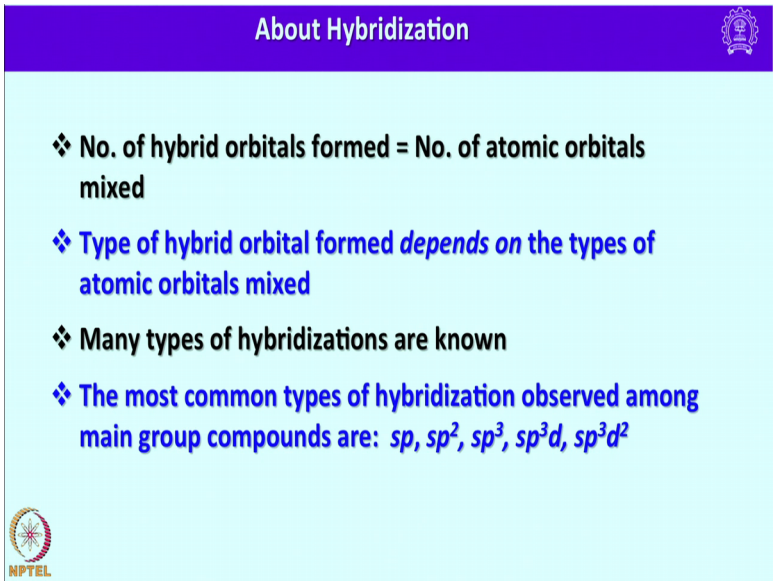

So, let us know little bit more about this hybridization concept, number of hybrid orbital form is equal to number of atomic orbital mixed; for example in carbon 1 s orbital and 3 p orbital that is 4 arbitral mixing together to make 4 hybrid orbitals, the type of hybrid orbital form depends on the types of atomic orbital mixed and many types of hybridization are known, the most common type of hybridization observed among male group compounds are essentially sp for linear sp2 for trigonal planar, sp3 for tetrahedral sp3 d for trigonal bipyramidal, sp3 d2 for octahedral and sp3 d3 for pentagonal bi pyramidal geometries.

So, I have listed some hiberation schemes that are used in various examples, here most of the examples I have given are from the coordination compounds; however as and when I come across such molecules while discussing main group chemistry, I would use valence bond theory to explain their bonding. So, here for linear 1 can use sp in case of trigonal planar sp2 tetrahedral it is sp3 and tetrahedral it is sp3 and square base in pyramidal.

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Hybridization Schemes for the σ-bonding frameworks of different configuration of ligand donor atoms.

CN	Arrangement of donor atoms	Orbitals hybridized	Hybrid orbital description	Example
2	Linear	s, p_z	sp	$[Ag(NH_3)_2]^+$
3	Trigonal Planar	s, p_x, p_y	sp^2	$[HgI_3]^-$
4	Tetrahedral	s, p_x, p_y, p_z	sp^3	$[FeBr_4]^{2-}$
4	Square Planar	$s, p_x, p_y, d_{x^2-y^2}$	sp^2d	$[Ni(CN)_4]^{2-}$
5	Trigonal bipyramidal	$s, p_x, p_y, p_z, d_{z^2}$	sp^3d	$[CuCl_5]^{3-}$
5	Square based pyramidal	$s, p_x, p_y, p_z, d_{x^2-y^2}$	sp^3d	$[Ni(CN)_5]^{3-}$
6	Octahedral	$s, d_{xy}, d_{yz}, d_{zx}, d_{z^2}, d_{x^2-y^2}$	sp^3d^2 OR^b d^2sp^3	$[Co(NH_3)_6]^{3+}$
6	Trigonal prismatic (TP)	$s, p_x, p_y, p_z, d_{zx}, d_{yz}$, $s, d_{xy}, d_{yz}, d_{zx}, d_{z^2}, d_{x^2-y^2}$	sp^3d^2 sd^5	$[ZrMe_6]^{2-}$
7	Pentagonal bipyramidal	$s, p_x, p_y, p_z, d_{xy}, d_{x^2-y^2}, d_{z^2}$	sp^3d^2	$[V(CN)_7]^{4-}$
7	Monocapped Tp	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{z^2}$	sp^3d^3	$[NbF_7]^{2-}$
8	Cubic	$s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{xz}, f_{xyz}$	sp^3d^3f	$[PaF_8]^{3-}$
8	Dodecahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{xy}, d_{yz}, d_{xz}$	sp^3d^4	$[Mo(CN)_8]^{4-}$
	Square antiprismatic	$s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}$	sp^3d^4	$[TaF_8]^{3-}$
	Tricapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{xz}, d_{z^2}, d_{x^2-y^2}$	sp^3d^5	$[ReH_9]^{2-}$

Rarely we come across among main group elements sp3 d and trigonal prismatic, we have 2 options pentagonal bi pyramidal we have 1 option, in case of octahedral only in case of coordination compounds we have 2 options, that is the sp3 d2 as well as d2 sp3 and when it is sp3 d2, we call it as outer orbital complex in case of d2 sp3 we call it inner orbital complex or low spin complex.

The outer orbital complexes are also known as high spin complexes. So, we have pentagonal bi pyramidal geometry sp3 d2 and mono capped trigonal prismatic geometry sp3 d3 and we have cubic geometry and also dodecahedral geometry and square ant prismatic geometry and tricapped trigonal prismatic geometry. So, the most of the hybridization we come across besides, this we also have interesting hybridization comes as sd3 and all those things they come exclusive in coordination compounds probably, if I happen to give another lecture series on coordination compounds and ergonomically compounds, I will be elaborating.

All these things in more detail and prior to utilizing this hybridization concept we should be familiar with the shape and orientation of the orbitals, that we are using in hybridization s is spherical is symmetrical and we know the with a relative orientation of px py and pz orbitals, I have shown in their axis assuming the vertical axis is y axis here.

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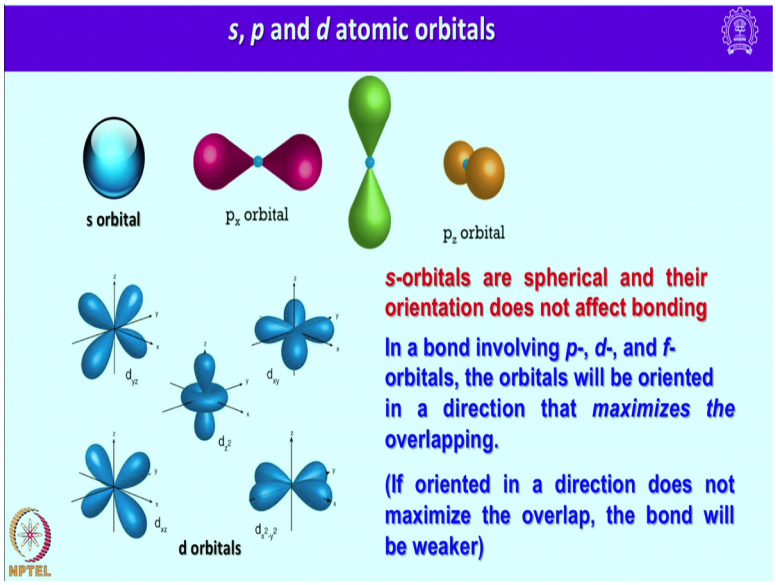

Also I have shown here 5d orbitals they are dx y dy z dx z dx square minus y square and dz square, in a bond involving p d and f orbitals the orbitals will be oriented in a direction that maximizes the overlapping 1 should remember this 1 I repeat again in a bond involving p d and f orbitals, the orbitals will be oriented in a direction that maximizes the overlapping. If oriented in a direction does not maximize the overlap the bond will be weaker; that means, repeat again if oriented in a direction that does not maximize the overlap the bond will be weaker.

So, just to show the difference between VSEPR theory and valence bond theory, I have given 2 examples, the example I have shown here to compare and see the difference between VSEPR theory and VBT is ammonia the pyramidal molecule.

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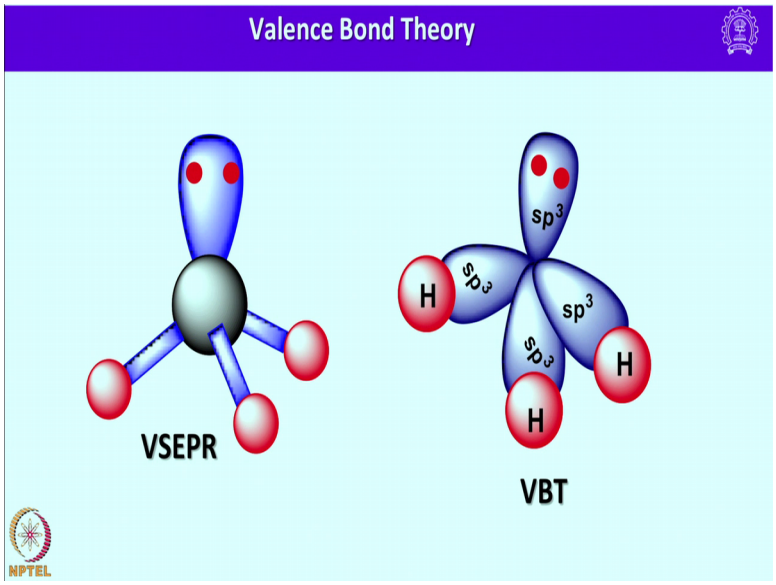

You can see this is trigonal planar geometry that can be seen from VSEPR theory with lone pair is occupying the fourth position, where the same one can draw using valence bond theory hydration concept; that means, in case of nitrogen what happens 1 nitrogen s orbital and 3 p orbital will combine together to form 4 sp 3, out of that 1 3 sp 3 orbitals will be having one electron each, whereas one sp 3 will have 2 electrons that is responsible for making ammonia as a Lewis base; this how one can visualize and also understand the difference between VSEPR as well as VBT ok.

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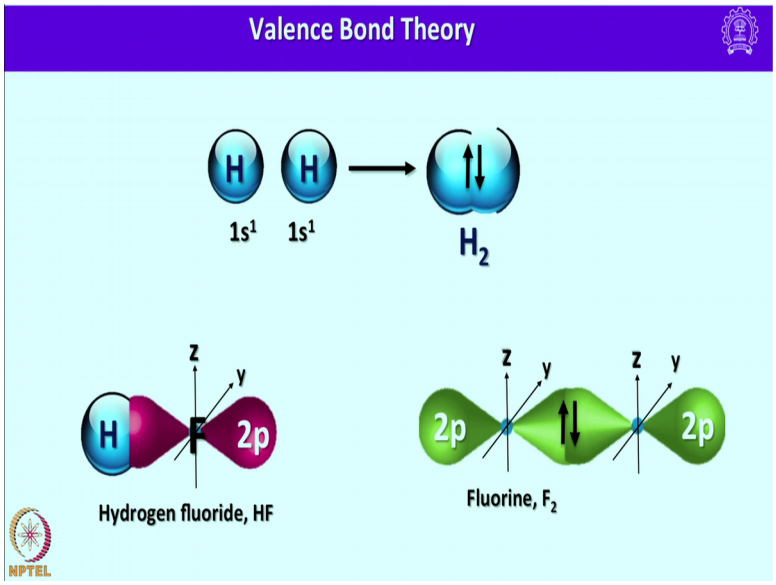

So, let us look into the formation of as simple as h 2 molecules. So, 1 s 1 orbital of 2 hydrogen atoms combine together to form hydrogen molecule and hydrogen fluoride in this case what happens 1 s 1 orbital of hydrogen with one of the 2 p orbital; that means, essentially if you just look into the fluorine, we have the electronic configuration of fluorine is of course, in case of h we have 1 s 1 electronic configuration in case of fluorine.

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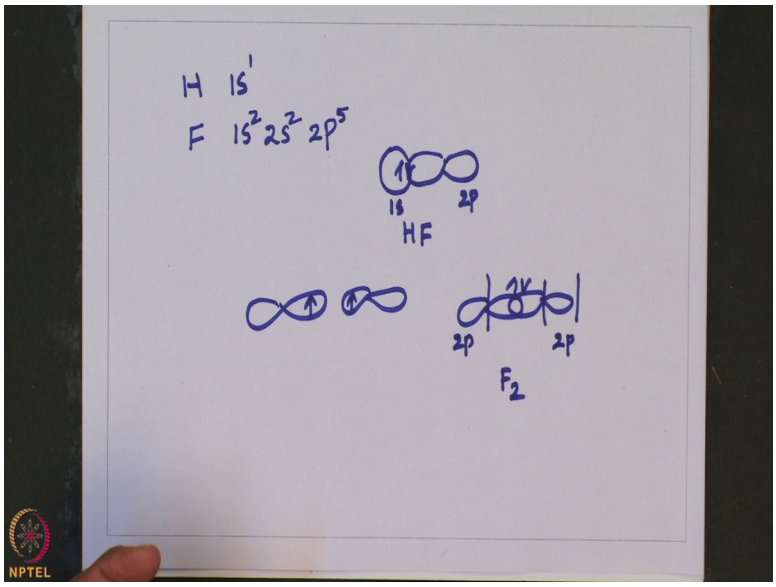

What we have is 1 s 2, 2 s 2 and 2 p 5, one electron combines with this 1 s orbital of hydrogen to form this hydrogen fluoride this is 2 p and this is 1s. So, this is how well here 1 can explain using this is very simple, probably we can we can go to little bit more complicated examples and see how hybridization happens and how they are disposed towards various positions in various geometries.

Now, this is about formation of fluorine in case of formation of fluorine molecule basically what happens, we have 1 2 p orbital having one electron and another one is there with another essentially they these 2 will overlap in this fashion and these 2 electrons will be placed here and this is how you can explain the formation of f 2 molecule. So, this is the 2 p orbital and this is 2 p orbital of course, a better picture is shown in the slide. So, let us consider now hybridization concept to begin with let us look into sp hybridization, for sp hybridization let us consider a main group example of alkaline earth metal halide that is Becl 2 beryllium dichloride.

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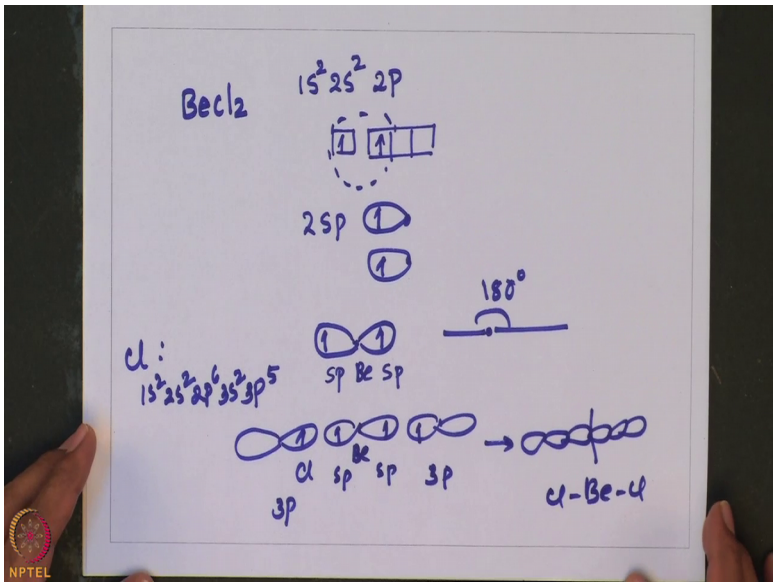

First what we should do is we should write the hybridization, before writing the hybridization we should write the electronic configuration of the central atom this is 1 s 2, 2 s 2, so that means, essentially this is the valence orbital and we have 2 electrons in s orbital and we do not have any electron in p orbital. So, prior to the formation of Becl 2 this s electron will be promoted to one of the p orbitals something like this, now both of them have one electron. So, they combine together to form 2 sp hybrid orbitals something like this having one electron each.

So, now we have 2 sp hybrid orbital on beryllium each one having one electron and now these will be aligned linearly like this. So, that angle between them is 180 degree. So, I have not started combining with chlorides, but this is how sp orbitals are oriented in case of beryllium prior to the formation of Bec l2. So, now, we have chlorine 3 p orbital of course, one can write the electronic configuration for chlorine also 1 s 2 2 s 2 2 p 6 3 s 2 and 3 p 5. So, we have one electron in one of the 3 p orbitals. So, that is coming here and that will come and orient in this fashion, this is beryllium and one more will come here like this is sp this is the sp and this is 3 p. So, this would leads to the formation of this beryllium bond.

So, this is how using valence bond theory especially hybridization concept, you should be able to write the structure of beryllium dichloride that is linear with angle between Becl angle being 180 degrees.

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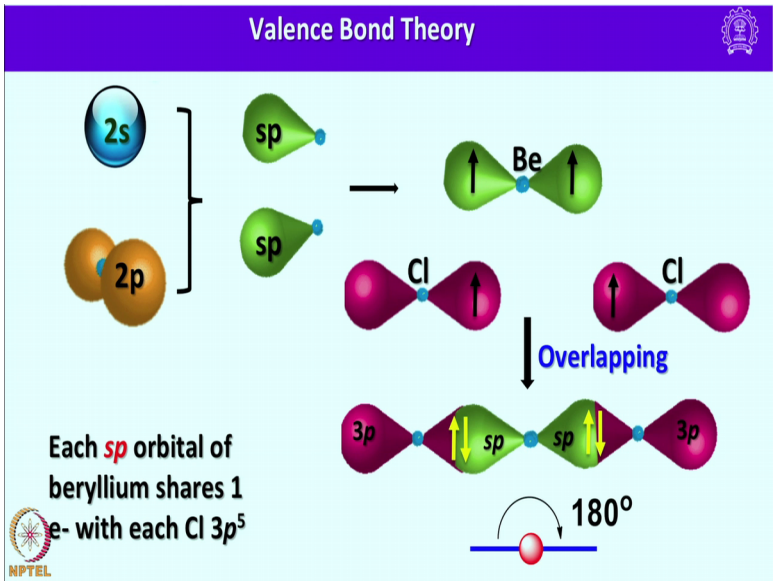

So that means, s p mixing takes place here. So, you can visualize that one here. So, 2 s and 2 p orbital combine together to generate 2 sp hybrid orbitals, now these 2 sp orbitals will orient in this fashion prior to the formation of are interacting with 2 chloride ions. Now 2 chloride ions from come here in this fashion and eventually they combine together to form Becl 2. So, this is how you can represent using hybridization concept or valence bond theory, the bonding in beryllium dichloride angle is 180 degrees.

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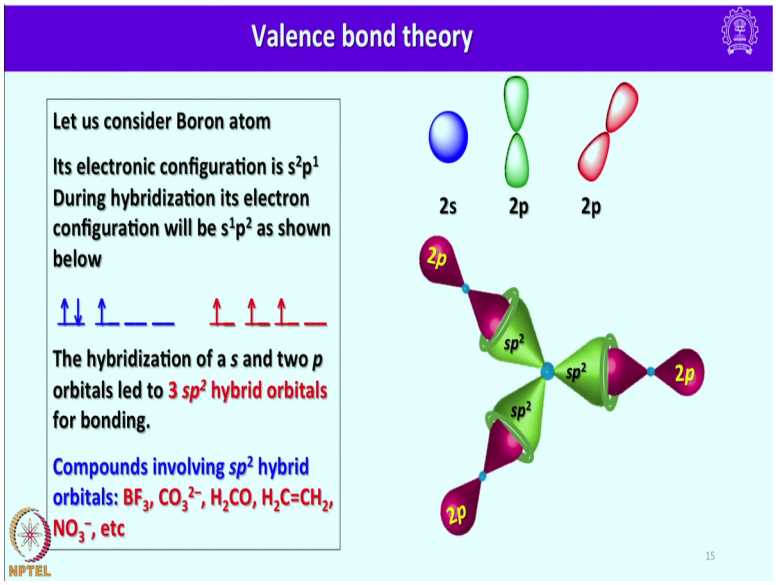

So, let us look into the boron atom, in case of boron atom this is another way of writing the electronic configuration and showing the hybrid orbitals for example.

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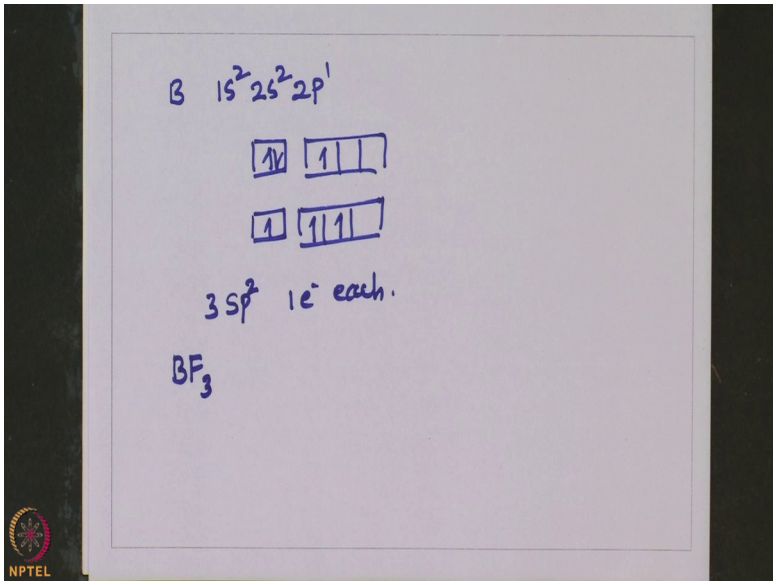

If you look into the boron electronic configuration it is 1 s 2 2 s 2 2 p 1 that is; that means, we have 3 electrons in it is valence shell. So, boron 1 s 2 2 s 2 2 p 1. So, this is how the electronic configuration is there in the ground state, prior to the mixing what happened this electron is promoted to the one of the empty p orbitals like this, now another p orbital do not have any electron. So, this s will combine with these 2 p orbitals to form 3 sp 2 orbitals with 1 electron each ok.

So, example you can consider bf 3, now each sp 2 having 1 electron from boron will combine with one of the 2 p orbitals having 1 electron to form 3 bf bonds so and of course, just I am showing you how s and 2 p orbitals are mixing here to form 3 sp 2 orbitals and this how 3 sp2 orbitals will be oriented with angle between them being 120 degrees; that means, it essentially orients in such a fashion to give a trigonal planar geometry; now as I mentioned 2 p orbits of 3 fluorine atoms will come and interact with 3 s p 2 orbits of boron having 1 electron each to form 3 bf covalent bonds and with an angle of 120 degree that is f bf angles are 120 degrees.

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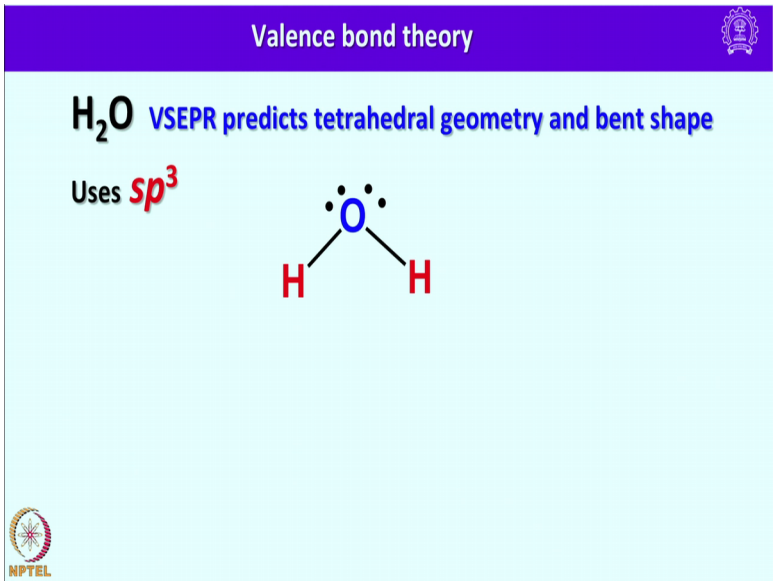

Let us look into the structure of water in water we have 1 O and 2 H are there and of course, each s hydrogen has 1 s 1 electron and 2 electrons are coming oxygen electronic configuration is 1 s 2 2 s 2 2 p 4 prior to the hybridization.

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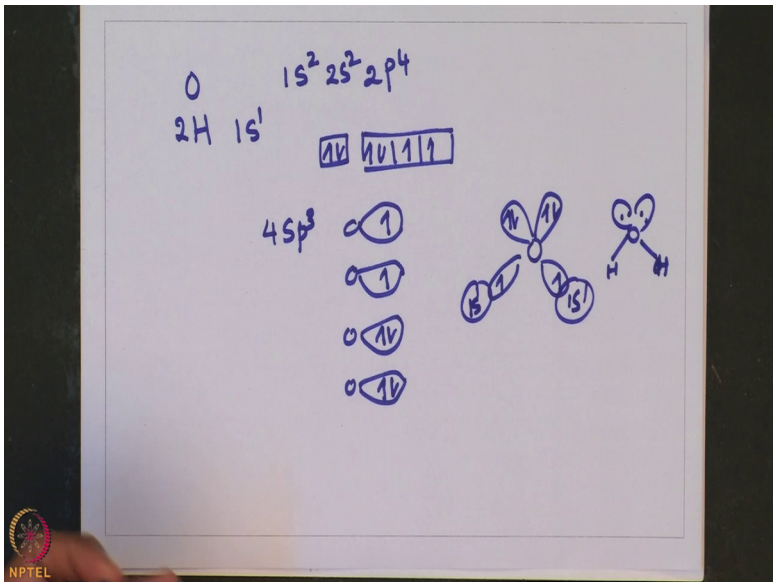

This is how it looks like 2 electrons here 1 electron here and 1 electron here. So, here when this s and these 3 p orbitals are mixed together it generates 4 sp 3 hybrid orbitals, with 2 having 1 electrons and 2 having 2 electrons; these 4 orbits are disposed towards

the 4 corners of a regular tetrahedron, that means let me write o here this is 1 this is 1 this is 1 and this is 1 these are all having 1 electron and these 2 are having 2 electrons.

So, now this will interact with 1 s one of hydrogen to form OH bonds and we have this lone pairs. So, here the geometry is again at oxygen is tetrahedral and the shape of water molecule according to VSEPR theory or valence bond theory it is bent or v shape.

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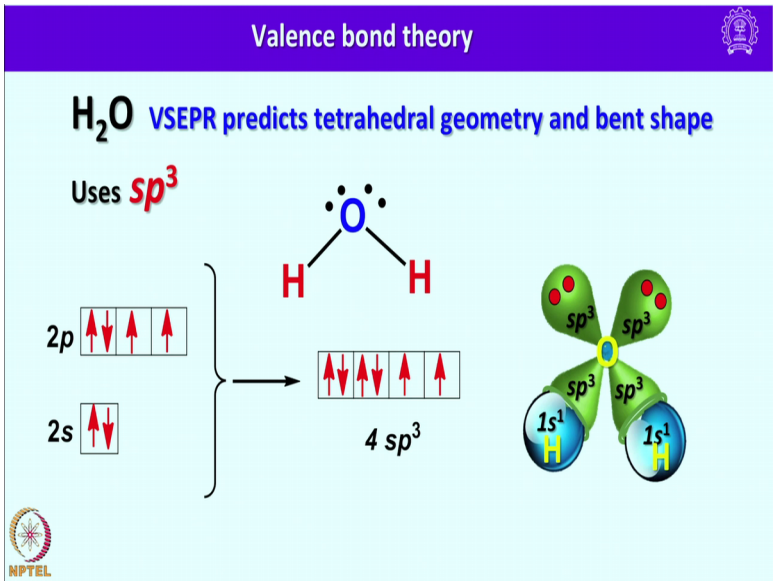

So, this how you can see or you can visualize the formation of H2O that is water, by utilizing 4 sp 3 orbitals of oxygen out of which 2 have 2 electron each and they remain as lone pairs and 2 sp 3 having one electron each will combine with 1 s 1 orbital of hydrogen to form 2 OH bonds, so that you can explain satisfactorily the bonding in water molecule. So, let me stop here in my next lecture I will continue with the higher hybridization and several more examples.

So, thank you very much.