

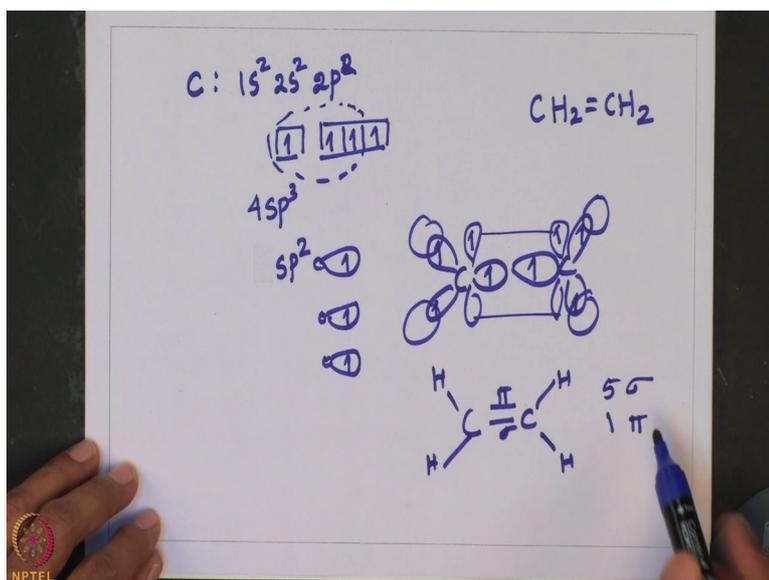
Main Group Chemistry
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Lecture – 08
Structure and Bonding aspects: Valence Bond Theory

Welcome to M.S.B lecture series on the chemistry of main group elements M.S.B stands for M.S.Balakrishna, in my last lecture while discussing Valence Bond theory I mentioned about the geometry and shape of water molecule. Now let me continue from where I had stopped let us look into the fundamental molecule that was used by Linus Pauling to explain the hybridization concept that is methane I was supposed to begin with methane since I wanted to go in the sequence I started with the first beryllium dichloride because it has a SP hybridization and then I discussed about SP 2 and also a discussion about SP 3 hybridization in case of water molecule where we have 2 bonded pair and 2 lone pairs.

Now, let us consider methane and in methane we have carbon as well as hydrogen carbon electronic configuration is $1s^2 2s^2 2p^2$.

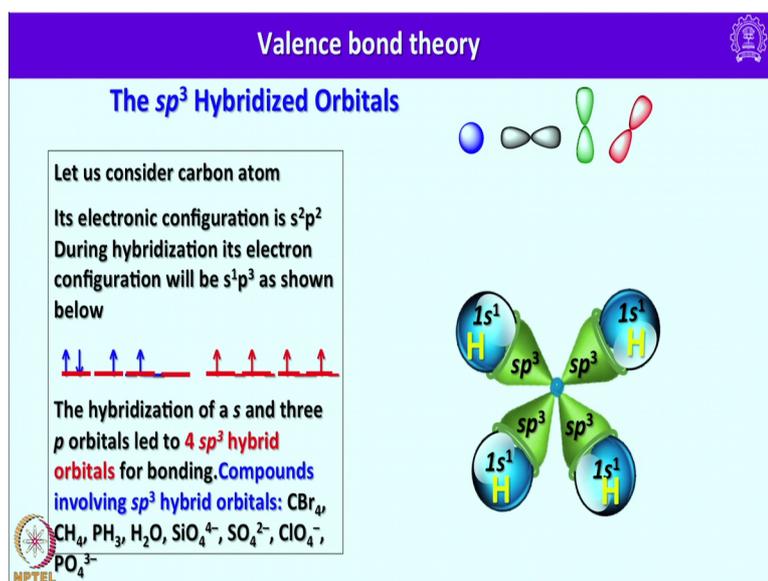
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So, prior to the hybridization this one of the S electron is promoted to the P orbital to have $S^1 P^3$ electronic configuration, now these 4 orbitals will combine together to form 4

SP³ hybrid orbitals having one electron each and now they are disposed tetrahedral and each SP³ with one electron would combine with 1s¹ orbital of 4 hydrogen atoms to form 4 CH bonds you can see here.

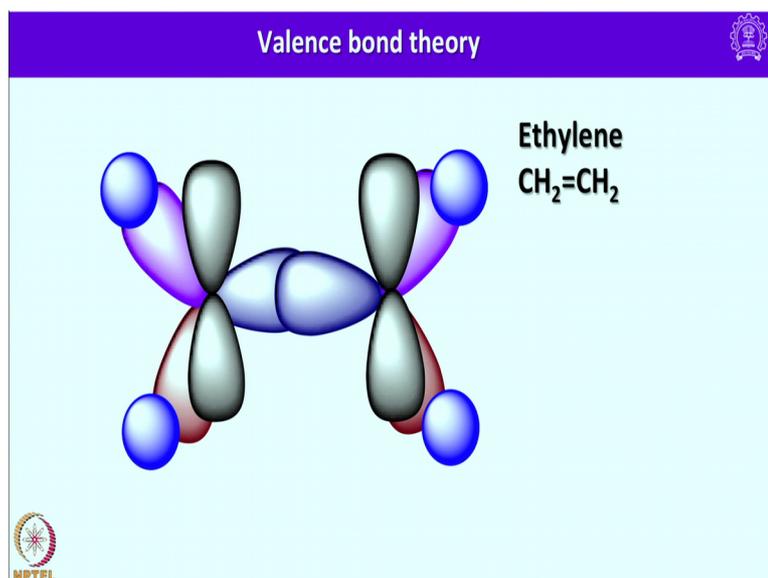
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So, SP³ hybrid 4 orbitals are disposed in this fashion and now they combine with 4 hydrogen atoms to form 4 CH bonds and this is a highly symmetric and tetrahedral molecule having the bond angles of 109.5 and I have also listed many other examples all tetravalent carbon compounds whether it is tetrabromomethane tetrafluoromethane all show SP³ hybridization besides this one molecules having one lone pairs such as ammonia PH₃, H₂O, SiO₄⁴⁻, SO₄²⁻, perchlorate in all central atoms poses this is SP³ hybridization and they have tetrahedral geometries.

You can always make an attempt to write in the same way for the rest of the molecules I have shown in the slide.

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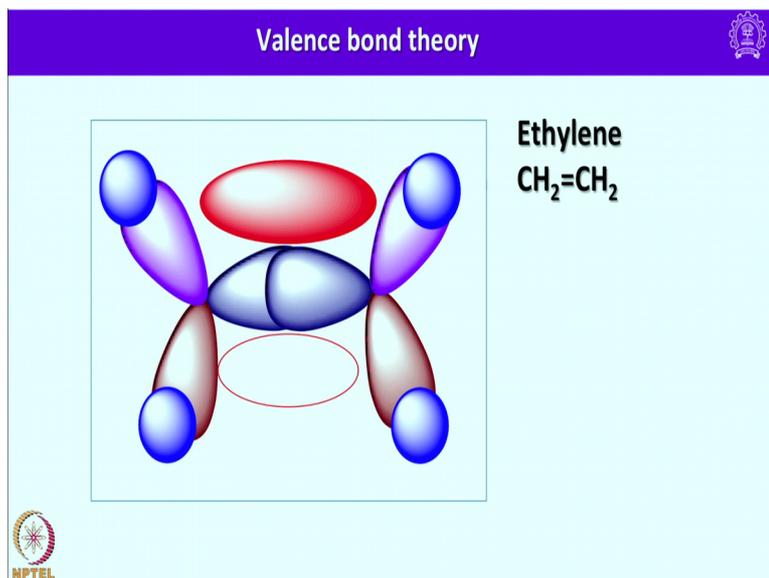


So, let us look into ethylene in case of ethylene the slightly different here once the electron is promoted to 1 of the empty P orbital now 1 of the P orbital is not utilized only 2 P orbitals and 1S orbital will combined together to form SP 2 orbitals having 1 electron each like this. So, these are at an angle of 120 so; that means, 2 carbon atoms would position in this fashion. So, these 3 this 3 are SP2 hybrid orbitals having 1 electron each and these terminal 2 here and 2 here 4 SP 2 orbitals with 1 electron will combine with hydrogen atom in this fashion to make 4 covalent bonds.

Now, we have this empty orbitals there at orthogonal to the SP 2 plane, they have one electron each now these 2 will orient in this fashion you to form a pi bond; that means, they interact in this fashion to form pi bond as a result what happens in case of this 1 we have a sigma bond and we have a pi bond and here this 2 are covalent bonds for example, in this ethylene molecule we have 1 2 3 4 5, 5 covalent bonds are there and 1 pi bond is there, this also covalent bond, 5 sigma bonds and 1 pi bond is there you can see this one in the in this slide here.

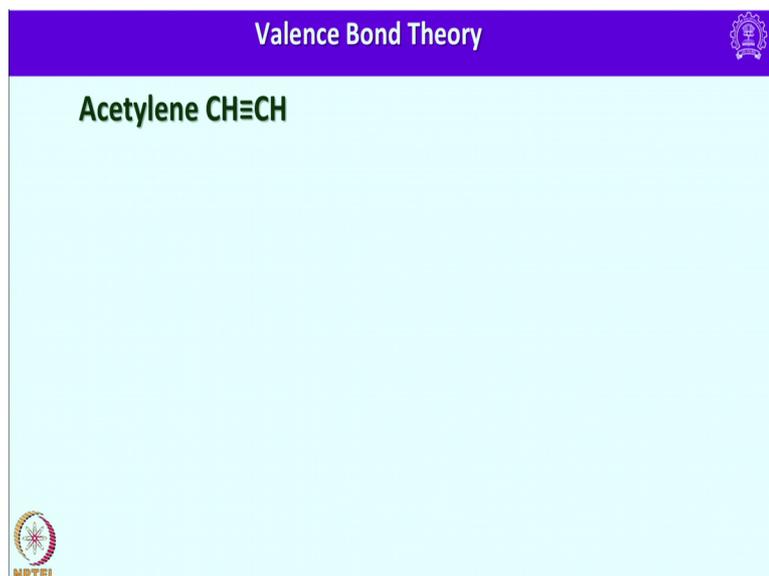
So, this how SP 2 are oriented and now the terminal ones are combined with 4 hydrogen atoms and now we have 2 P orbitals on each carbon having 1 electron they combined together to form pi bonds.

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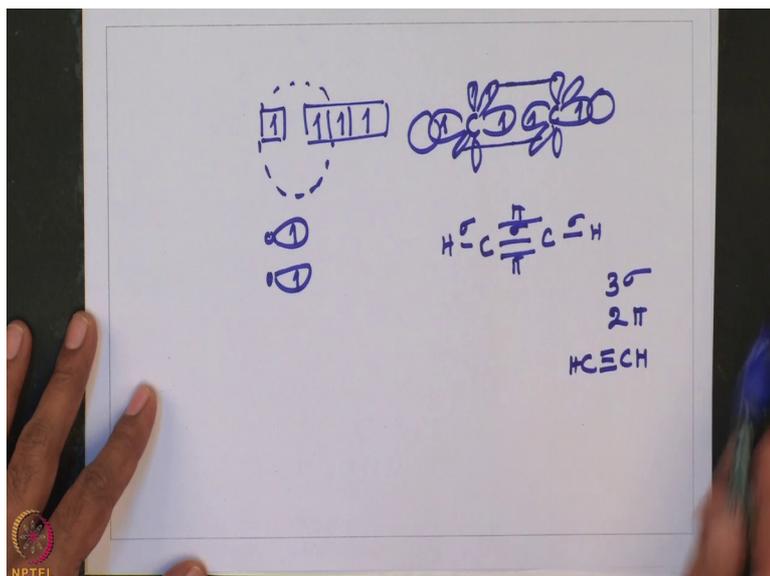
So, this how we can expand bonding in case of ethylene molecule using this vibration concept or valence bond theory.

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Let us look into one more example Acetylene again in Acetylene carbon promotes one of the S electron to the P orbital and we have a situation like this.

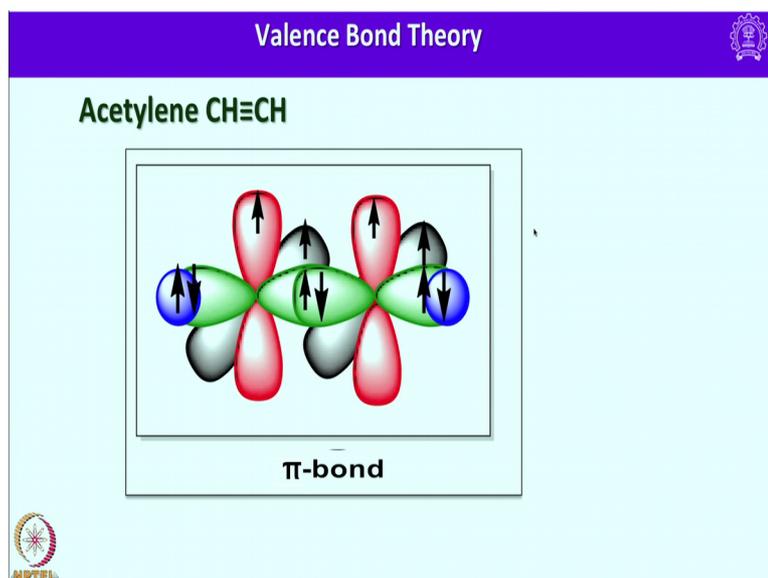
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So, now, we have 4 orbitals having 1 electrons each, in case of acetylene carbon utilizes only 1 of the P orbital preferably P z and these 2 are combined together to form 2 SP orbit having 1 electrons each they are oriented in this fashion. So, they have 1 electron each here, 1 electron here as usual this one of the SP from each carbon will combine with hydrogen atom and now we have 2 P orbitals and each one having 1 electron each and now they are overlapping in this fashion.

So, now what we have is in case of acetylene we have 1 sigma bond, 1 sigma bond, another sigma bond and 1 pi bond, another pi bond so; that means, in this one we have 1 2 3 sigma bonds and 2 pi bonds. So, you can explain bonding in Acetylene.

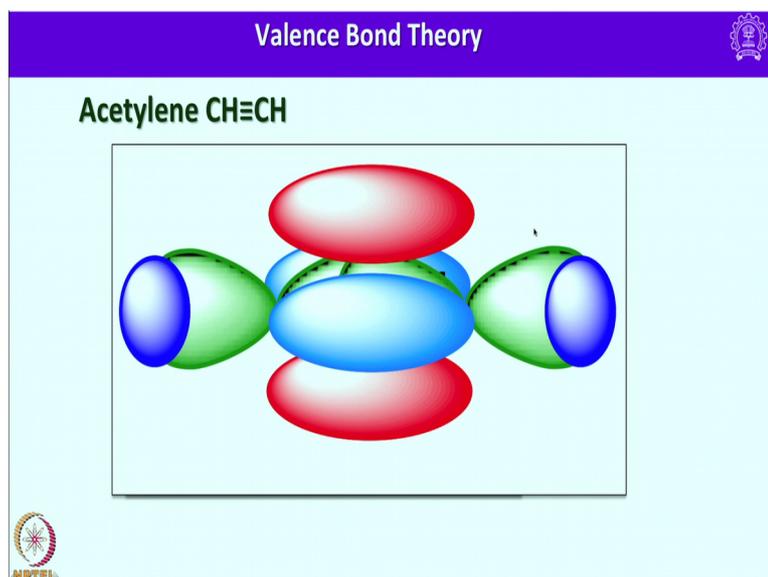
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We have arranged 2 SP orbital having 1 electron each and unutilized 2 P orbitals having electron each and they come close to each other to establish a bond and now this how you can explain the bonding now only I have some sigma bond in this one at 3 sigma bonds I have shown.

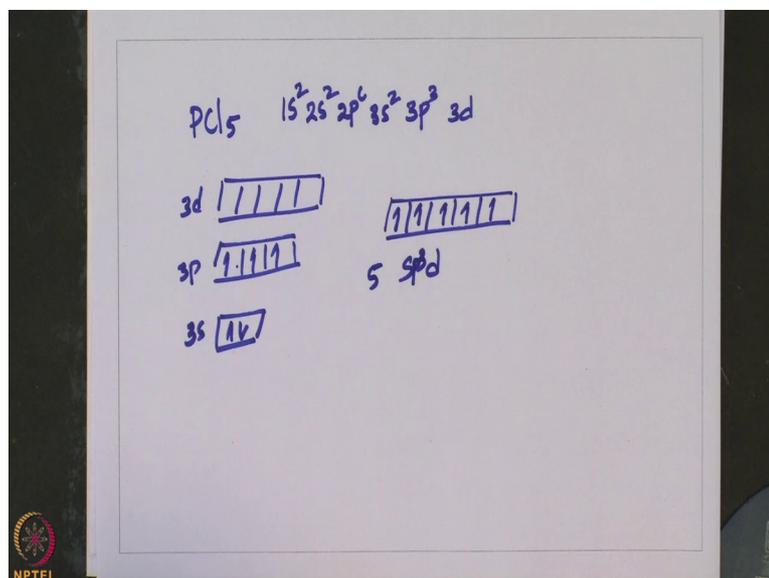
Now, these 2 P orbitals and these 2 P orbitals will interact together similarly this 2 P orbital and this 2 P orbital interact together to form 2 pi bonds having 2 electrons each pi bond begins and you get acetylene molecule like this.

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So, this how you can explain the process of 3 bonds between 2 carbon atoms in acetylene let us look into higher hybridization.

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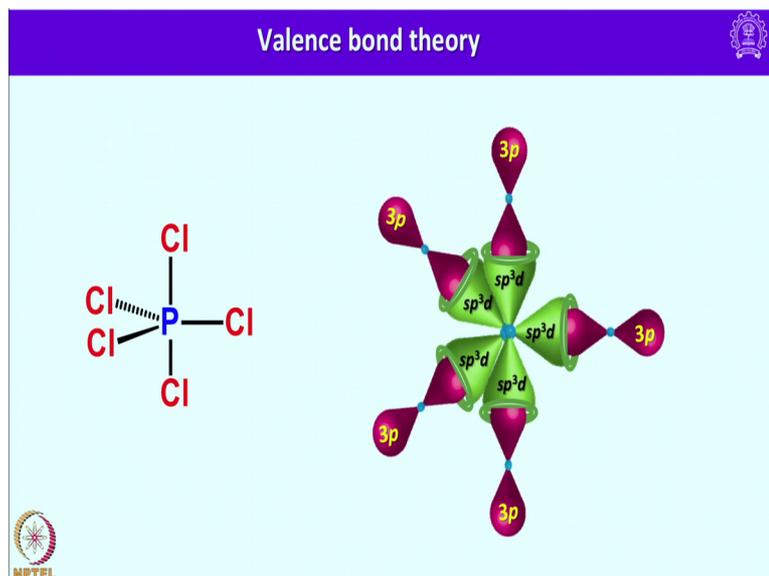


Let us consider the example of PCl_5 , PCl_5 central atom is P and from Vsepr theory we have predicted it to be having trigonal bipyramidal geometry, here we had 10 pairs of electrons. So, that is giving 5 steric number and all are bonded, when the steric number is 5 the geometry is trigonal bipyramidal.

So, let us look into it from Valence Bond theory, let me right of course, here we have to utilize d orbitals and in case of phosphorus the electronic configuration is $1s^2 2s^2 2p^6 3s^2$ and $3p^3$. So, here we have 3 d orbital also, but that is empty. So, let me write in this fashion empty orbital of high energy this is 3 d next we have 3 P orbital having 1 electron each and then we have 3S having 2 electrons.

So, now basically this S orbital and this P orbital one of the d orbital will combine together to form sp^3d hybridization 1 2 3 4 5. So, 1 2 3 4 5 electrons are there these 5 electrons will occupy 5 sp^3d hybrid orbitals and these 5 sp^3d hybrid orbitals are oriented in a trigonal bipyramidal fashion let me show you in that one in the next slide. So, this is how the structure looks like for PCl_5 we all know.

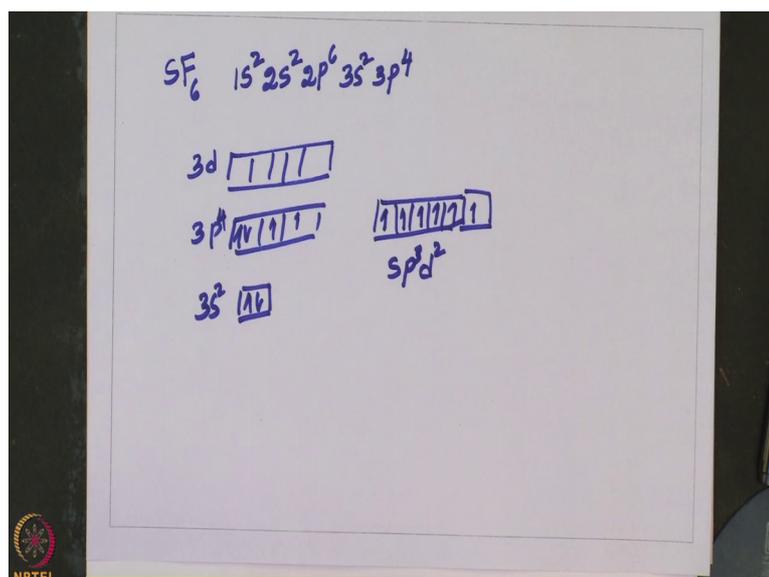
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Let us see how, this hybrid orbitals orient and combine with 3 P orbital of chlorine.

So, this is how this 5 sp^3d hybrid orbitals are oriented and now they combine with 3 P orbitals to form PCl_5 . So, you can explain very conveniently the structure of PCl_5 using hybridization concepts. So, let us look into another example of group 16 elements that is sulphur appearing at maximum of state that is SF_6 sulphur hexafluoride.

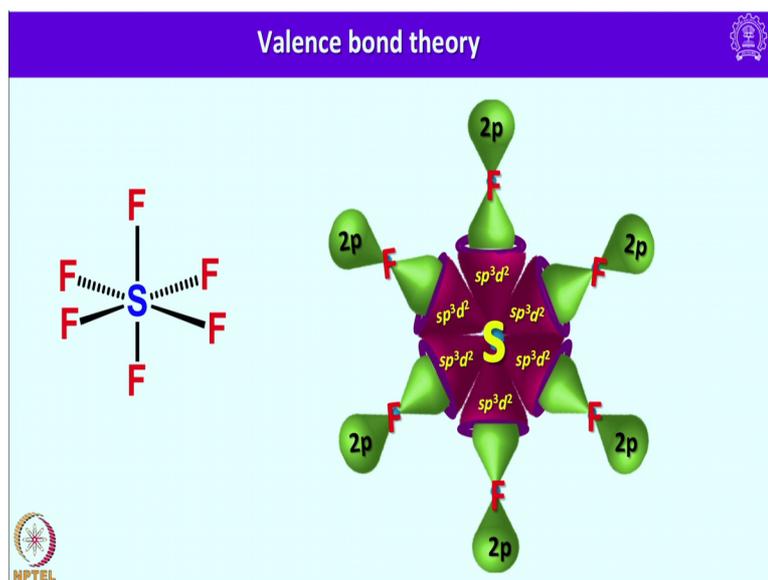
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So, let me write again the electronic configuration of sulphur $1s^2$ it is below oxygen $2s^2 2p^6 3s^2 3p^4$ if we do not remember the electronic configuration we should try to remember to which group it belongs and then also we should remember what name it is given to the group if a particular name exists for a particular group like noble nitrogen, chalcogen in the fashion.

So, we know that sulphur is below oxygen, its electronic configuration is same as that of oxygen once you know that one you should be able to write the electronic configuration this is $1s^2 2s^2 2p^6 3s^2 3p^4$ now again we have high energy d orbitals like this we have 4 electrons here and then in we have 2 electrons now these 1 2 3 4 5 since we have 2 extra electrons they can be promoted to 2 d orbitals as a result what happens it utilizes 2 more orbitals to form 6, 1 2 3 4 5 and 6 hybrid orbitals composite of 1 S and 3 P and 2 d. So, 1 is to 3 is to 2 and now each one has 1 electron each.

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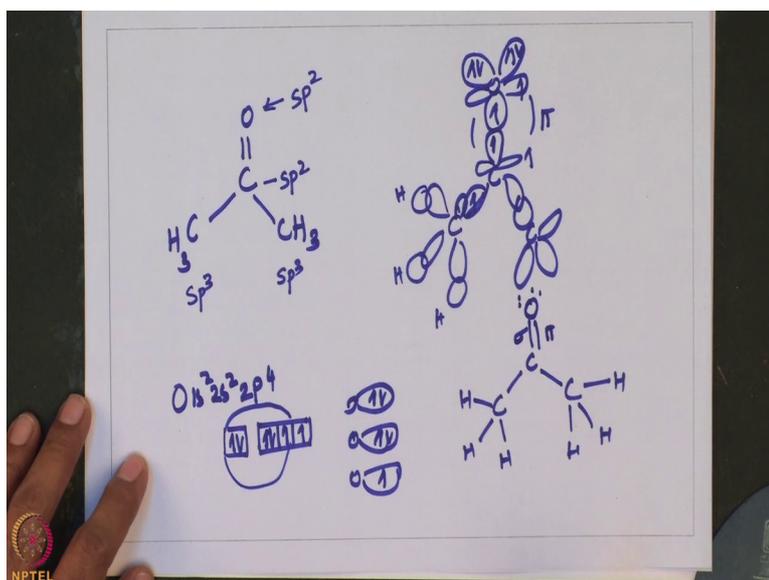


So, there are 6 orbitals are there, they are disposed to the 6 corners of an octahedron. So, this is the structure of SF_6 it is octahedral and this how 6 sp^3d^2 orbitals are disposed along z minus z x minus x y minus y axis and now they combine with 6 2 P orbitals of fluorine atoms to form these octahedral molecules. Of course, here we are utilizing d orbital and say that they have the sulphur undergoes sp^3d^2 hybridization when we go to the molecular orbital it essentially gives a different combination of atomic orbital and different structure altogether of course, the geometries octahedral, but molecular orbital

depicts its formation in a different way I should tell you more about that one when you go to the group 16 chemistry.

Because SF_6 as well as $SiCl_6^{2-}$ they are called hyper valent molecules. So, I will elaborate about these things and also how we are utilizing the atomic orbitals to explain the bonding in SF_6 as well as $SiCl_6^{2-}$ while discussing the chemistry in the respective groups. So, let me take a simple example before I proceed further to make you familiar with the valence bond theory especially for poly atomic molecules let us take as simple example as acetone and let us try to look into the bonding of each carbon atom and also oxygen atom and describe the structure of the entire acetone molecule using hybridization concept.

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So, now let me first write the structure of acetone this is a structure of acetone here we have 4 atoms are there besides hydrogen, this carbon, this carbon, this carbon and then this oxygen and from the structure I have written you should be able to clearly see the kind of hybridization one can think of for each atom present here and this carbon should be of SP^3 in nature and this carbon should be a SP^3 in nature and this carbon should be of SP^2 in nature and this oxygen should be SP^2 in nature

So, let us see how that happens now without going into the electronic configuration since you are all familiar with electronic configuration what I will do is I will simply write the

corresponding hybridization and the corresponding orbital and I show the overlapping to describe the structure of this acetone molecule. So, here this one, this carbon has undergone sp^3 hybridization having 4 sp^3 orbitals with 1 electron each and 3 sp^3 orbitals will combine with hydrogen atoms and then this one will combine with one of the sp^2 and this will also combined with one of the sp^2 and one sp^2 is here. So, here and this carbon has undergone sp^2 . So, it has 1 electron here and one of the P orbital and then oxygen also undergone sp^2 hybridization so; that means, that you may not be familiar let me write in case of oxygen how to explain sp^2 hybridization.

In case of oxygen we have $2s^2 2p^4$ of course, $1s^2$ and now if this oxygen and ((Refer Time: 18:06)) sp^2 in that case what I should do is we have a situation like this. So, we have a situation 1 electron here, 1 electron here. So, here it undergoes sp^2 hybridization when it forms 3 sp^2 we should remember 2 of them have 2 electrons and one has 1 electrons so; that means, here essentially oxygen this 1 electron, 1 electron here and this are lone pairs 2 electrons are there and we have 1 P with this electron here and these 2 will combine together to form a pi bond.

So, essentially in case of acetone now I can write 1 CC bond, another CC bond and 3 H bonds, CH bonds and here 1 sigma bond and 1 pi bond and oxygen and lone pairs. So, no matter how complicated the molecule looks like if you start one at a time we should be able to write and describe the structure of any such molecules for example, we can take even bigger molecules and you can make an attempt to write in this fashion at to make yourself familiar with this hybridization concept.

So, let me introduce one more term that is often used in valence bond theory that is Bent's rule.

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Valence bond theory 

What is Bent's rule:

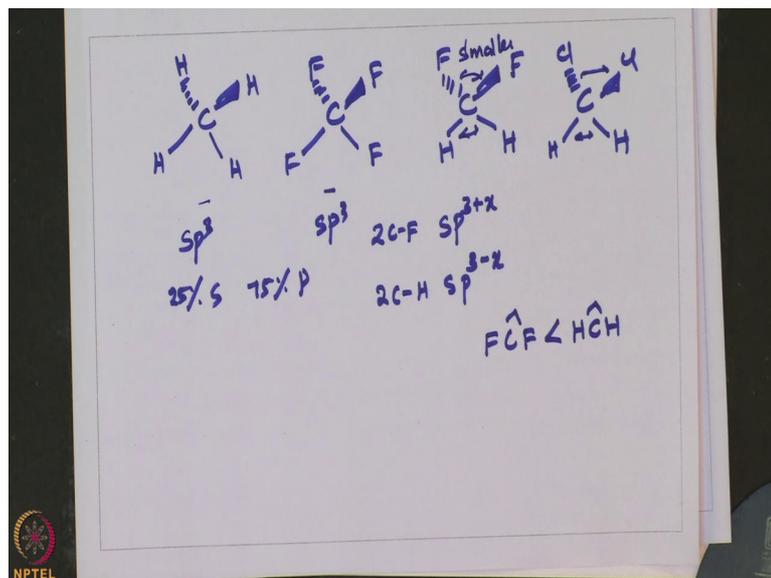
More electronegative substituents 'prefer' hybrid orbitals having less s-character, and more electropositive substituents 'prefer' orbitals having more s-character.

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What it says more electronegative substituents 'prefer' hybrid orbitals having less S - character that is more P character and more electropositive substituents prefer orbitals having more S - character that is having less P character; that means, if you consider a homoleptic poly molecule such as methane or tetrabromo methane we have sp^3 hybrid orbitals all are equivalent and each sp^3 has 25 percent S - character and 75 percent P character, but when we have heteroleptic molecules for example, dichloromethane, difluoromethane and here we can identify 2 different type of peripheral atoms born to carbon one of them is more electronegative another one is less electronegative or more electropositive.

So, in that case a bents rule comes very handy in explaining the bonding especially the variation in the bond angle. So, how to again I define the bents rule with this informationo, more electronegative substituents prefer hybrid orbitals having less S - character and more electropositive substituents prefer orbitals having more S - character. So, this is how you can explain bent rule then we can use these bents rules successfully to explain bonding in molecules such as methane or trifluoromethane or difluoromethane etcetera.

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Let us take CH_4 , I have given here 3 examples one is methane other one is tetra fluoro methane and the third one is difluoromethane it can be difluoromethane or even one can also write dichloromethane.

In all the 4 cases we are using SP^3 hybrid orbitals of carbon combining with either hydrogen or fluorine or fluorine corresponding orbitals to form these molecules. In case of methane and in case of tetra fluoro methane no issues all bonds are identical as a result still each SP^3 has 25 percent S character and 75 percent P character, but that is not the case when we go here.

So, here according to bents rule to safe bonds utilizes SP^3 orbitals having more P character and these 2 C H bonds utilizes orbitals having less P character or more S character; that means, I can write in this fashion 2 CF bonds utilizes SP^3 plus x and 2 CH utilizes SP^3 minus x; that means, here automatically you can see here in these cases P contribution is more where as in these 2 cases P contribution is less or in other words S contribution is more here and S contribution is less here.

So, what would happen on the overall bond angle if this anomaly exists, in case of S P 3 imagine if the P character increases you just imagine the combination of 3 P orbital in the absence of S it would be 90 degree with respect to each other because P_x P_y P_z are orthogonal to each other the angle between them is 90 degrees and if S character

decreases as a result what happens the angle will start decreasing it will come close to the 90 degrees.

On the other hand if s character increases it will go from 90 to the maximum tetrahedral angle of 109.5. So, with this information we should be able to write and predict the variation in the bond angle just simply based on the electronic of the atoms that are making the bond with the carbon. So, in this case we can see clearly that the FCF bond angles are lower smaller; that means, I can say FCF angles are smaller than HCH angles.

In fact, this is more pronounced in case of pyramidal molecules of phosphorus arsenic antimony for example, if you take PH_3 SbH_3 or AsH_3 or the corresponding trichlorides this bent rule is more pronounced again we can explain there by looking into the difference in electron negativity of these atoms and besides these one can also use some other means to explain this one that is simply looking into the electron negative difference between the central atom and the peripheral autumn.

So, I hope it is clear here. So, here SP^3 in case of CF and CH are different, in case of CF SP^3 has more P character, in case of here SP^3 has less P character, when the less P character is there angles are close to the tetrahedral are greater than 90 or in case of fluorine where the P character is more that is coming close 90 degrees. So, let us look into one example here.

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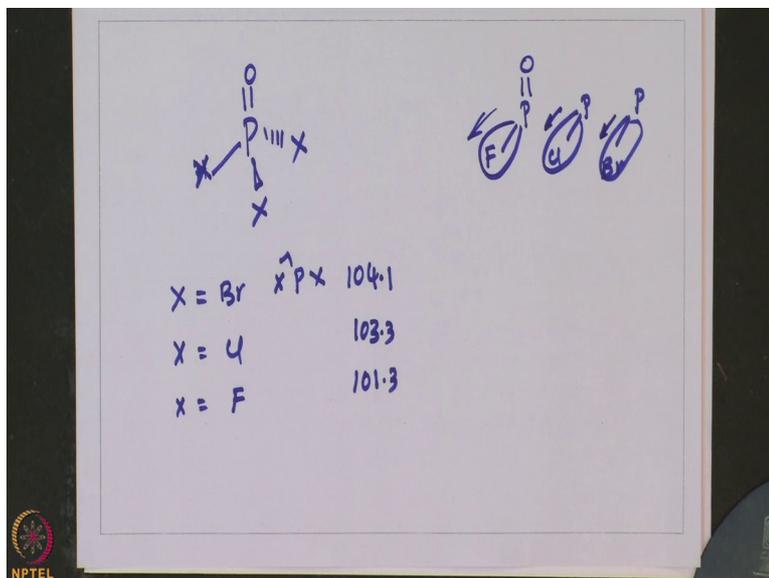
Ask a Question

Explain why the X-P-X bond angles for the series of POX_3 molecules decrease from X = Br (104.1°) to X = Cl (103.3°) to X = F (101.3°)



You can see that example given here why X P X bond angles for the series of POX 3 molecules this is POX 3 molecules.

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This is POX 3 molecule where X equals bromine, X equals Cl, x equals fluorine. So, here angles are given X P X angles are given here and in this case it is 104.1, 103.3 and 101.3.

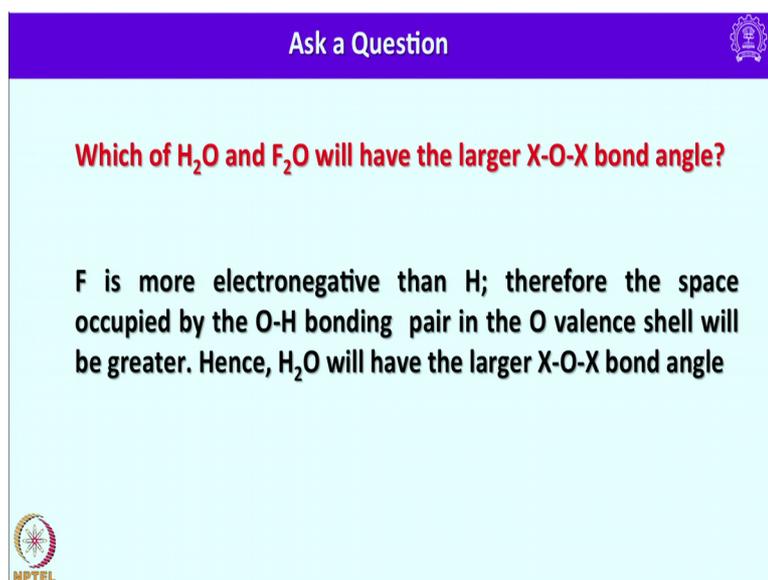
So; that means, angles are decreasing when you go from bromine to fluorine and the other hand angle is increasing when you go from fluorine to chlorine to bromine. So, again here same analogy one can use the electro negativity of the atoms are decreasing electro negativity of halide ions are decreasing as a result what happens that P character is increasing as a result when the P character is increasing when the P character is increasing the angle will decrease.

Of course, here all the angles are less than 100 here the bents rule may not be very precise to explain, but we can explain using the electro negativity difference between P and X here for example, in case of fluorine let us take this one here and let us also consider this chlorine and this bromine we can see the electro negativity this atoms fluorine chlorine bromine is decreasing when it is decreasing what would happens is the electrons stay almost midway between here and here.

So, in this 1 electrons are more towards fluorine and here it is less and here it is less; that means, as electron density coming more and more towards the peripheral atoms the angle start shrinking and the other end if the electrons are coming more and more towards the central atom angle will be increasing. So, with this analogy you can see that in this one since the electron density is more directed towards the fluorine. So, here not much electron density is there. So, the angle will shrink so, that it can give more space for this oxygen double bond on the other hand here it is less electronegative; obviously, you can expect angle to be a little larger and in this case angle can be even larger because little bit more electron density is going or less electron density is coming towards the halide ions.

So, you should be able to explain why this is happening in case of for XPX the trend can be explained.

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Ask a Question

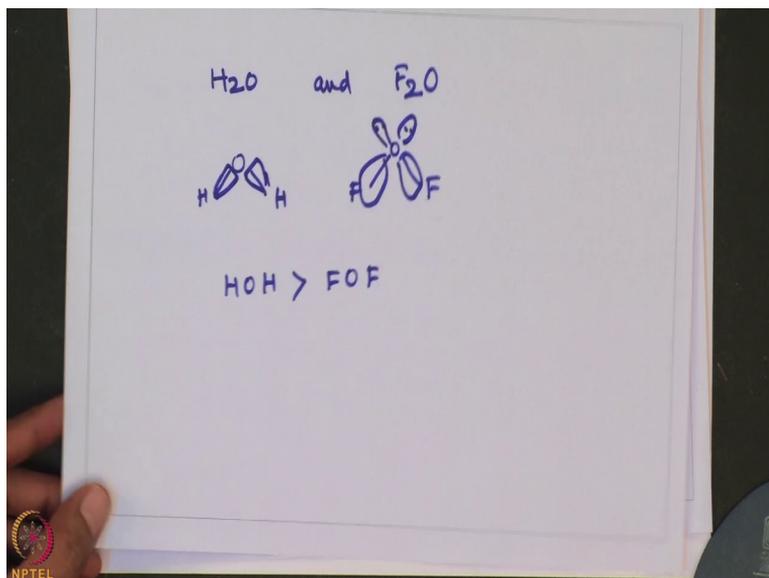
Which of H_2O and F_2O will have the larger X-O-X bond angle?

F is more electronegative than H; therefore the space occupied by the O-H bonding pair in the O valence shell will be greater. Hence, H_2O will have the larger X-O-X bond angle

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You can see here same example I have shown. So, essentially one can also analyze same thing in case of water and H_2O for example.

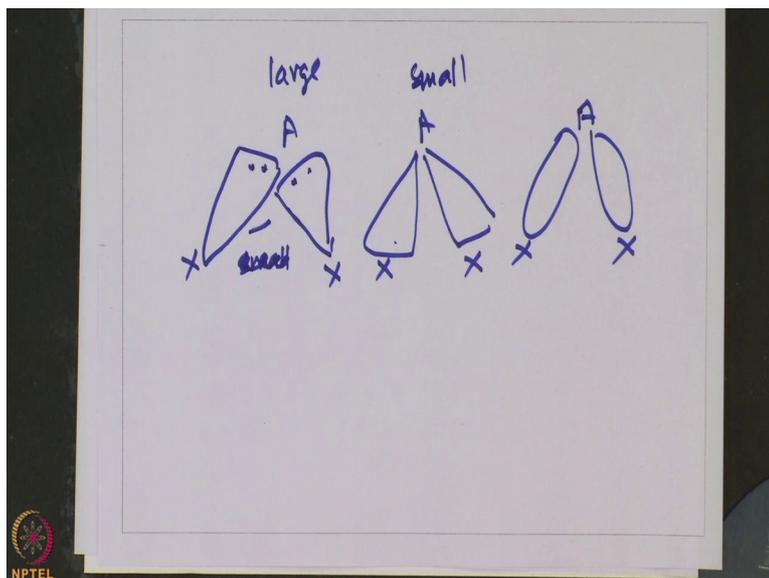
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If you want to look into the case of water and F₂O you should be able to tell which angle for example, if I write something like this you should be able to tell HOH and FOF which angle is larger this angle is larger and this is smaller because here the electron density is something like this. So, that since electron density drops towards fluorine atoms here angle shrink. So, that it can give more space for these lone pairs to minimize interelectronic repulsion.

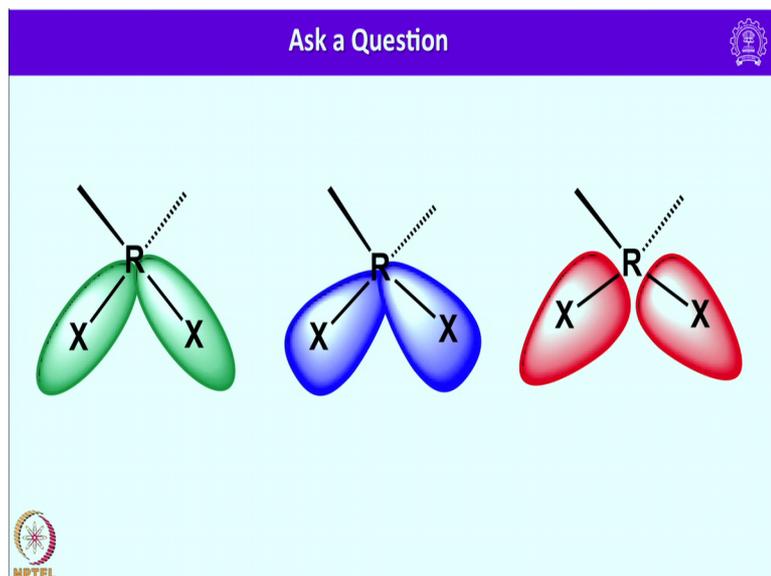
So, whereas here this angle will be little larger because the electron density is residing more on oxygen atom so; that means, now no matter what molecule is given simply by looking to the electro negativity difference between the central atom and peripheral atom you should try to remember 3 structures I am writing here.

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One is like this, one is like this and one is like this. So, here if electro negativity of A is more electrons will stay here as a result angle shrinks, angle will shrink small angle and here electron density is coming here. So, angle increases here in this case larger angle because lone pairs are at central atom it increases. So, last one, in this case the electron density is moving away from me, angle is small. So, here it is intermediate, just by looking into the electro negativity difference between the central atom and the peripheral atom you should be able to remember these 3 once you remember this things, you can see what is the consequence of this one and the bond angle.

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In the first case bond angle will be normal, in the second case bond angle will be larger, in the third case bond angle will be smaller. So, this how you can use Valence bond theory to almost understand the bond parameters such as bond distance and bond angle very clearly. So, now, I conclude valence bond theory of course, in my next class I will be telling you about the limitations we come across in valence bond theory and I will proceed to the molecular orbital theory. So, I have a pleasant reading.