Concepts of Chemistry for Engineering
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Lecture No. 17
Molecular orbital theory 5: Heteronuclear diatomic molecules

Next we are going to discuss heteronuclear diatomics with particular reference to HF and we will also talk about a carbon monoxide. In HF what happens is this.

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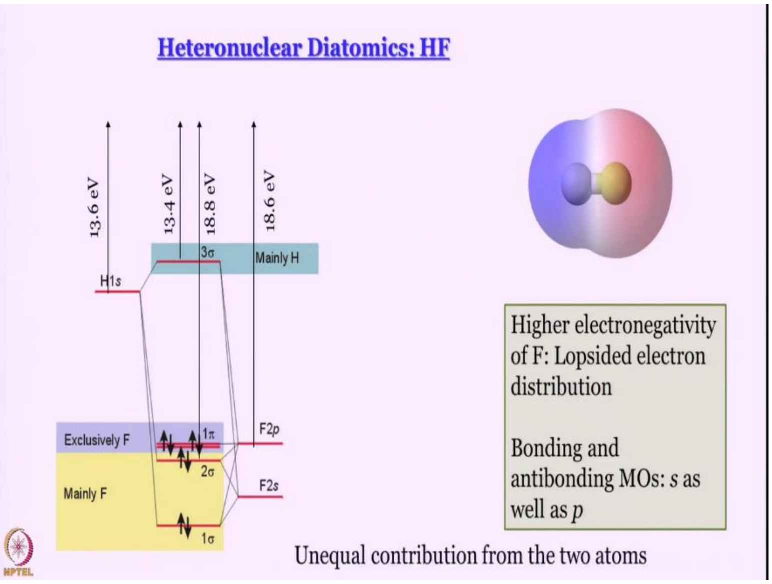

Heteronuclear Diatomics: HF

Higher electronegativity of F: Lopsided electron distribution

Bonding and antibonding MOs: *s* as well as *p*

Unequal contribution from the two atoms

Neglect the molecular orbitals for the moment. On the left-hand side we have shown hydrogen atom 1s orbital. On the right-hand side we have shown fluorine atom, 2s and 2p orbitals and that should raise questions. What is going on here? Why is it that energy of 2p orbitals for fluorine is so much less than the energy of hydrogen atom 1s orbital. Well, that is because you have so many more protons in the nucleus that electrons are sort of drawn in and the energy gets lower and lower as you go, as you make, as you go higher up the atomic number ladder.

So, for fluorine, you do not even consider the inner orbitals, 1s orbital. They are non-bonding. That means they do not participate in linear combination. You can think like that. And if you think of F2s and F2p and compare with H1s, first thing that I want to say is that we are considering the x, y, z, we are considering the internuclear axis to be the z axis.

So, when we want to discuss sigma interaction, it is the 2pz orbital of fluorine that is going to participate. 2px and 2py orbitals will remain on fluorine because on hydrogen atom there is no other orbital of sufficiently low energy that have comparable symmetries with 2px and 2py of fluorine. So, you can think of hydrogen atom like this. The only orbital available is 1s. Others are very high energy.

For fluorine, we have let us say 2px, 2py, 2pz. So, 2pz is like this. This is the sigma interaction that has taken place if at all. There will be 2s as well. We will see that. But now 2px is here, 2py is there. There is nothing like that at sufficiently low energy for hydrogen atom. So, this px and py orbitals do not participate in any linear combination for forming molecular orbitals these are called non-bonding orbitals and they stay on fluorine.

So, if you go back to the Lewis electron dot structure, you will remember that there are lone pairs on fluorine. So, these are your lone pairs. The only additional thing we are saying here is that, these lone pairs reside in px and py orbitals which are collectively now called the 1 π orbital. But remember, 1 π orbital here is actually non-bonding and localized on fluorine also.

What about the sigma orbitals? Well, sigma orbitals you see they do participate in a linear combination, because they have the right geometry, but energies are so much lower that this bonding orbitals that you get are mostly orbitals that have contribution from 2s and 2p orbitals of fluorine not so much from hydrogen atom 1s. And this 3 σ , the anti-bonding orbital here that resembles the hydrogen atom wave function very, very closely.

Why do, how do I know all this? I know this from ionization, for ionization energies, which is determined by something called photoelectron spectroscopy. It established that for HF, you have an ionization energy of about 18.8 eV, which is very, very close to the value of ionization energy for fluorine atom 2p. So, energetically, this diagram is correct. Whereas for 1s orbital of hydrogen atom, I hope you have not forgotten that the ionization energy is 13.6 eV. We get another ionization energy for HF at 13.4 eV, very close values, that is how this energy diagram of the molecular orbitals has been constructed.

So now, see, this orbital is close in energy to hydrogen atom 1s orbital. So, in the linear combination that you have, you have about 98 percent contribution from hydrogen atom 1s orbitals and 2 percent maybe from the orbitals of fluorine. So, it is predominantly hydrogen orbital. Similarly, for bonding and non-bonding I said exclusively F, even for bonding this is small, maybe

2 percent contribution from hydrogen atom 1s orbital. But these are mainly made up by atomic orbitals of fluorine 2s and 2pz atomic orbitals of fluorine.

So, what we encounter is a lopsided electron distribution. Look at the electron configuration. Where are the electrons? I have one electron from hydrogen, seven electrons from fluorine. And once you start filling them in, there is no memory. You just fill them in in the increasing order of energy for molecular orbitals. So, all the electrons are in either bonding or non-bonding orbitals which are either mainly fluorine orbitals or exclusively fluorine orbitals. What does that mean?

That in HF the electron density is very strongly lopsided, it is very strongly localized over fluorine and hydrogen gets a very small share. What is it? It is a polar covalent bond, is not it? And an extreme case of that would be ionized bond. So, this is something nice that we learn from our discussion of HF that only orbitals with comparable energies and compatible symmetries would participate in linear combination to give you the molecular orbitals. So, if any of these conditions is not fulfilled, it will not happen.

So, in case of HF you have predominantly fluorine like bonding orbitals, exclusively fluorine like non-bonding orbital and predominantly hydrogen like anti-bonding orbitals. And since there is no electron in the anti-bonding MO, the electron density that is there is very strongly lopsided towards, we get a polar covalent bond.

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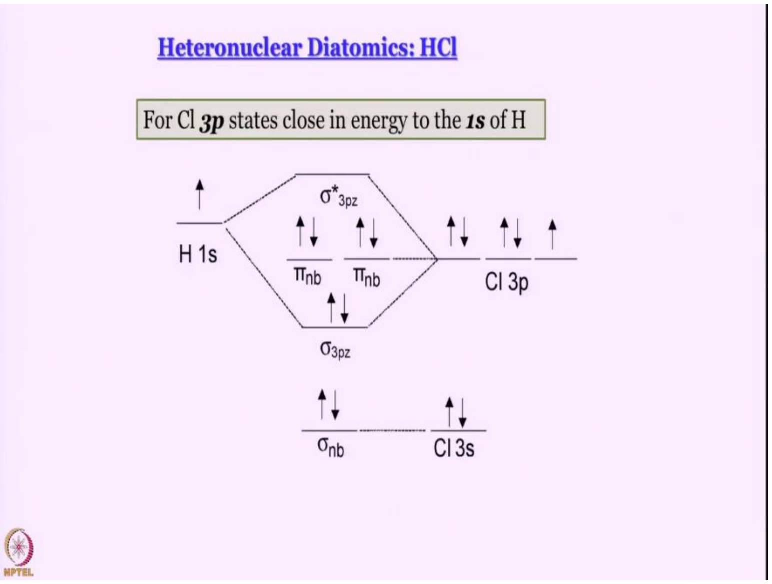
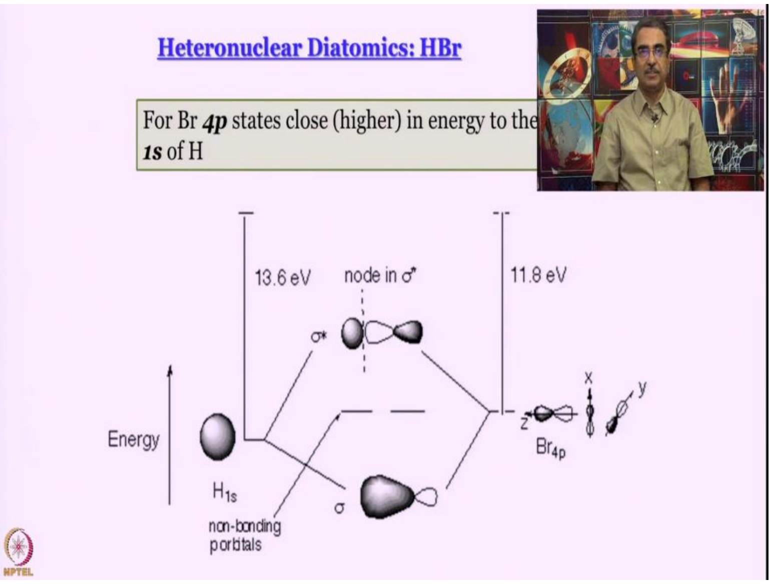


Heteronuclear Diatomics: HCl

For Cl ***3p*** states close in energy to the ***1s*** of H



Heteronuclear Diatomics: HBr

For Br ***4p*** states close (higher) in energy to the ***1s*** of H

You can perform exactly a similar discussion for HCl. The only difference being that in the case of HCl the orbitals that have comparable energy with hydrogen atom 1s orbital are actually 3s and 3p orbitals and for HBr where you need to consider this 4p orbital. This is how you handle this problem.

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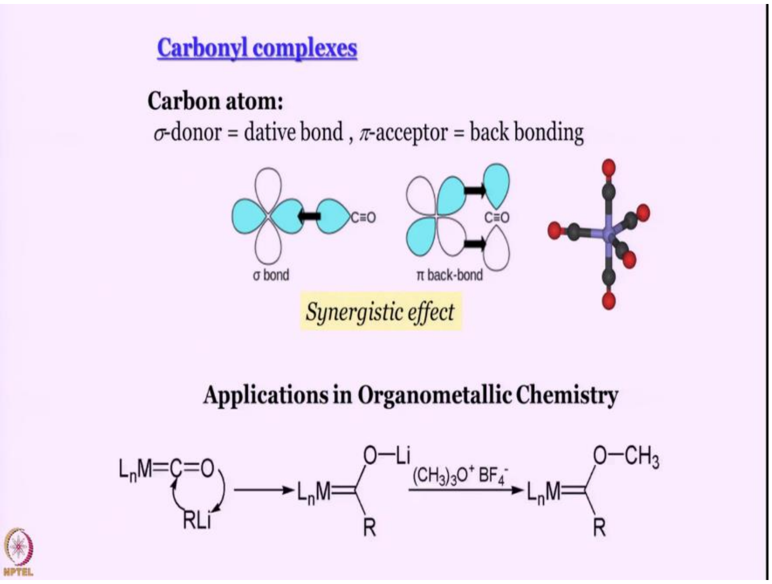

Carbonyl complexes

Carbon atom:

σ-donor = dative bond , π-acceptor = back bonding

Synergistic effect

Applications in Organometallic Chemistry

The second part of our discussion of heteronuclear diatomic molecules is on carbon monoxide. Carbon monoxide, I think I am not really sure if you are going to study this in the remaining part of the course, but perhaps you know already that carbon monoxide is a very good complex, very good ligand for metal ions, they can form carbonyl complexes, is also been established that this carbon atom can act as a sigma donor, it forms a dative bond or coordinate bond and it can also accept as a pi acceptor that is called back bonding and that gives rise to a synergistic effect. This is something we learn in inorganic chemistry.

Why does it happen? Why is it that it is a carbon atom and not an oxygen atom that likes to donate the electron in a sigma fashion? And why is it that it can sustain back bonding? And it is very important also because carbonyl complexes do have lots of applications in organometallic chemistry like this.

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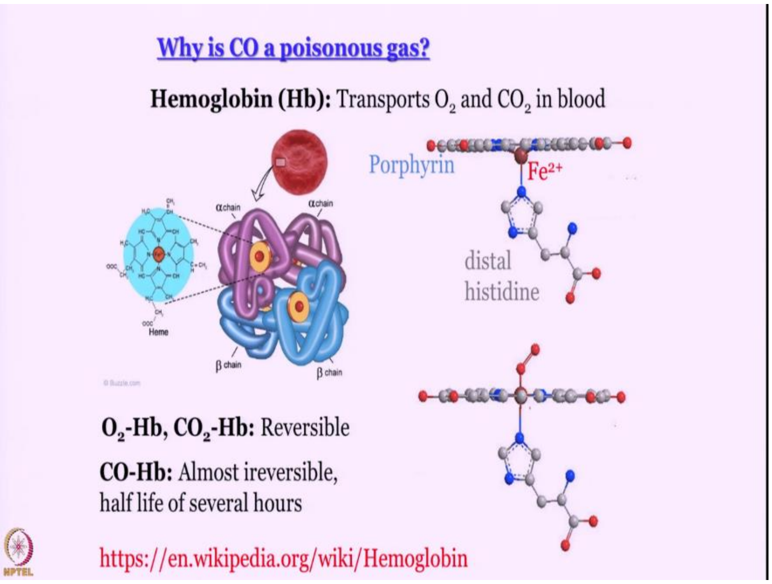

Why is CO a poisonous gas?

Hemoglobin (Hb): Transports O_2 and CO_2 in blood

O_2-Hb, CO_2-Hb: Reversible

CO-Hb: Almost ireversible,
half life of several hours

https://en.wikipedia.org/wiki/Hemoglobin

And carbon monoxide is a poisonous gas. Why, because this is a cartoon representation of hemoglobin which transports oxygen and CO_2. At the heart of hemoglobin, you have this iron, ferrous iron. And what happens is that in regular hemoglobin, this is a structure of hemoglobin. There is this heme unit where you have porphyrin and the porphyrin ligates the metal ion from four sides in a square planar fashion.

So, the axial positions are available. One axial position is usually taken up by solvent molecules is believed. The other one is taken up by this amino acid from the protein side-chain, distal histidine amino acid moiety from the protein chain. And the way it transports oxygen and carbon dioxide is that oxygen and carbon dioxide bind in the other axial position by driving out the solvent molecules.

The problem with carbon monoxide is that when carbon monoxide comes and binds like this, it does not want to leave. It forms a very, very strong complex carbonyl hemoglobin and that is why hemoglobin is blocked. It cannot participate in oxygen transport and the organism died out of lack of oxygen, asphyxia.

So, CO_2 and O_2 form reversible complexes with hemoglobin, whereas carbon monoxide forms an almost irreversible complex in half-life of several hours and by the time the damage is done. That is why it is poison. The question is why?

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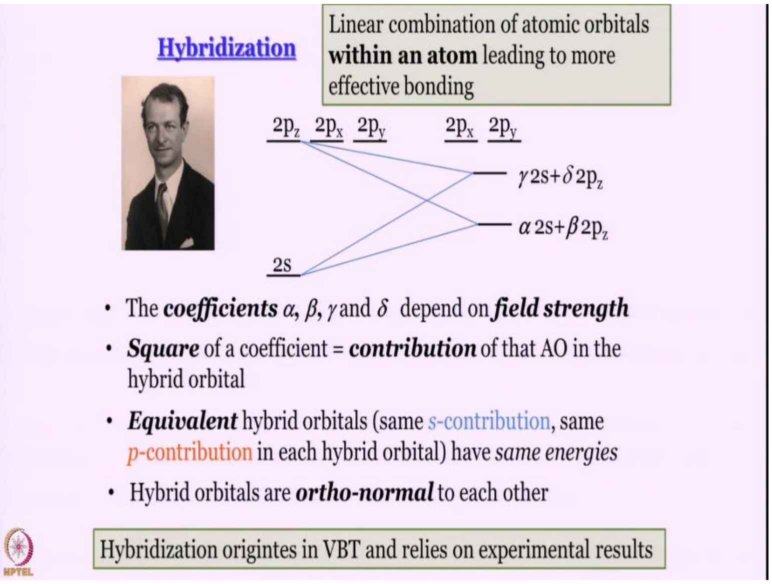

Hybridization

Linear combination of atomic orbitals **within an atom** leading to more effective bonding

- The ***coefficients*** α, β, γ and δ depend on ***field strength***
- ***Square*** of a coefficient = ***contribution*** of that AO in the hybrid orbital
- ***Equivalent*** hybrid orbitals (same *s*-contribution, same *p*-contribution in each hybrid orbital) have *same energies*
- Hybrid orbitals are ***ortho-normal*** to each other

Hybridization origintes in VBT and relies on experimental results

To explain this one uses the concept of hybridization proposed by Linus Pauling. Hybridization means you mix two orbitals to generate two new orbitals.

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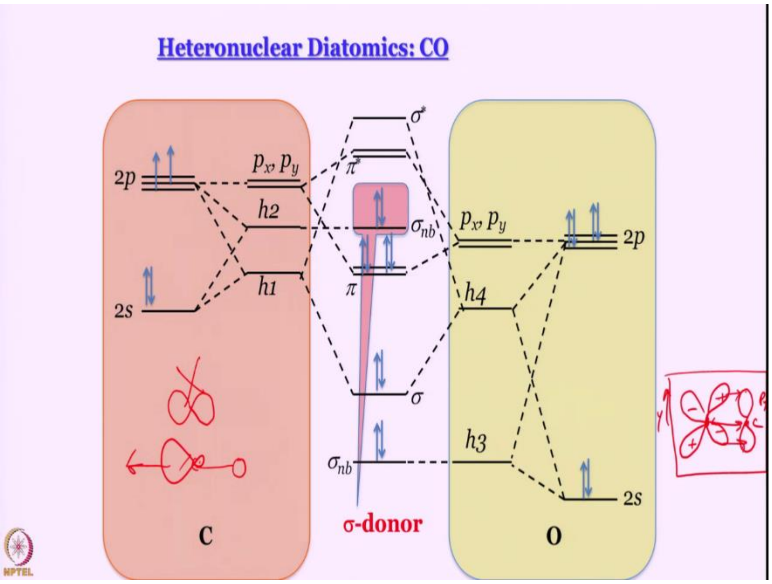
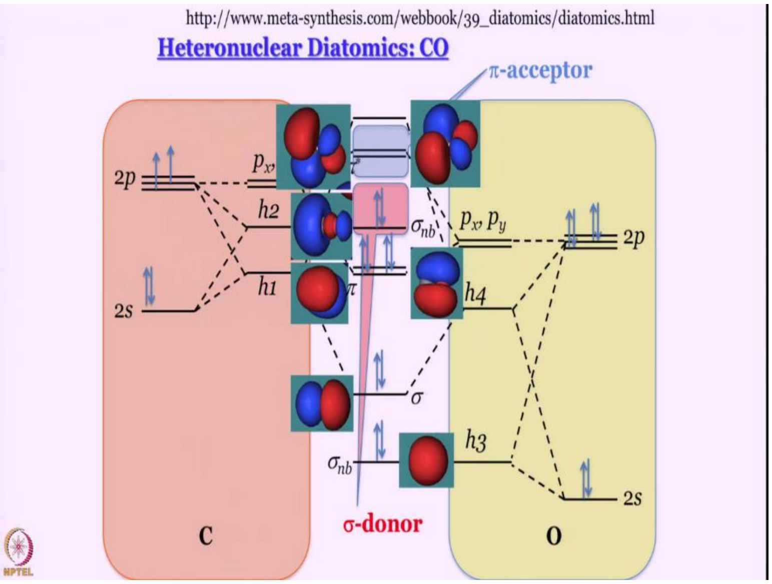


Heteronuclear Diatomics: CO



http://www.meta-synthesis.com/webbook/39_diatomics/diatomics.html

Heteronuclear Diatomics: CO

And I will tell you this model and I tell you what the problem is also. So, the assumption here is that in carbon there is sp mixing and you form h1 and there is another sp mixing which gives you h2 two hybrid orbitals and both are σ kind of orbitals. Similarly, for oxygen, you get a lower line h3 hybrid orbital, a higher line h4 hybrid orbital. Do you see the problem here? The problem is in our earlier discussion of homonuclear diatomics we had said that in the case of oxygen there is no sp mixing because the energies are too far apart. In this case then why is it that we have a sp mixing? There is no good answer.

You can try to argue that the other atom is carbon and CO is actually isoelectronic with N_2, but I think there is a lot of controversy over this. We use this model because it helps us understand things, but please be aware that it is not a completely accepted model. Now, what happens? See, h3 has such low energy. So, even though symmetry is right, it cannot form a bond. It remains as a non-bonding orbital. I keep forgetting about the px and py for chaps.

Similarly, h2 has too high energy so that remains a nonbonding orbital. The only difference is that the h2 orbital is a non-bonding orbital on carbon and the h3 orbital is a non-bonding orbital on oxygen. Next, what happens? h1 and h4 are both sigma kind of orbitals, the energies are close enough. So, they can give you σ and σ^* molecular orbitals. What about your px and py? They are going to give you the π and π^* molecular orbitals. So, this is believed to be the electron, the energy diagram for carbon monoxide.

Now, let us fill in the electrons, four electrons from carbon. Remember we are neglecting the n equal to 1 shell altogether; we are only talking about the valance shell. So, 4 electrons there and 6 electrons for oxygen. When we fill them, again there is no memory. How do we fill them? The lowest energy MO has two electrons. The higher one has two.

Next, we have two degenerate π bonding orbitals. So, there we are going to accommodate not one electron pair, but actually two electron pairs. How many are taken care of 2, 4, 6, 8. Two more are there. Where will it go? It will go to this, σ non-bonding. So, this is the electron configuration by our proposed model.

Now think what is the σ non-bonding? Remember HF how some orbitals were lopsided on hydrogen and some orbitals were lopsided on F. Here also the σ_{nb} is actually lopsided. Why, because σ_{nb} is a non-bonding orbital on the carbon atom. So, it is very safe to say that these two electrons are actually on carbon and they are highly directed. So, that is why they make carbon atom a good sigma donor.

At this point, you might want to ask, what is the need of invoking hybridization at all. You could have done this using pz, yes. But the shape of pz is like this. And shape of a hybrid orbital is like this. The major loop and minor loop is very small and the nucleus is in the minor loop. So, now, this is your carbon monoxide. This is carbon. This is oxygen. Carbon is known to be a strong sigma donor. So, it is not very unreasonable to expect that it is using a hybrid orbital which is very highly localized rather than a regular pz orbital. That is why we invoke hybridization here. And that is why carbon monoxide is a good sigma donor through the carbon atom.

How about this back bonding, well, back bonding, if you remember the figure takes place like this. You have a d orbital, very bad diagram, you have a d orbital like this. Now, remember this is z-direction. So, if I have, and let us say this is y-direction or something. If we have py then it can form a pi overlap. What is this? The center is the metal. What is this? This is carbon. If the orbital is like this and it is not even a p orbital, remember, it is a π^* orbital so it will bend towards this way. Now you can have π kind of interaction.

In fact, if I show you the orbitals, this is what they are supposed to look like. This kind of an orbital makes CO a good sigma donor through the carbon atom. This kind of orbital, remember, they are also localized on carbon atom makes carbon atom a good π acceptor and that is how the synergistic effect takes place.

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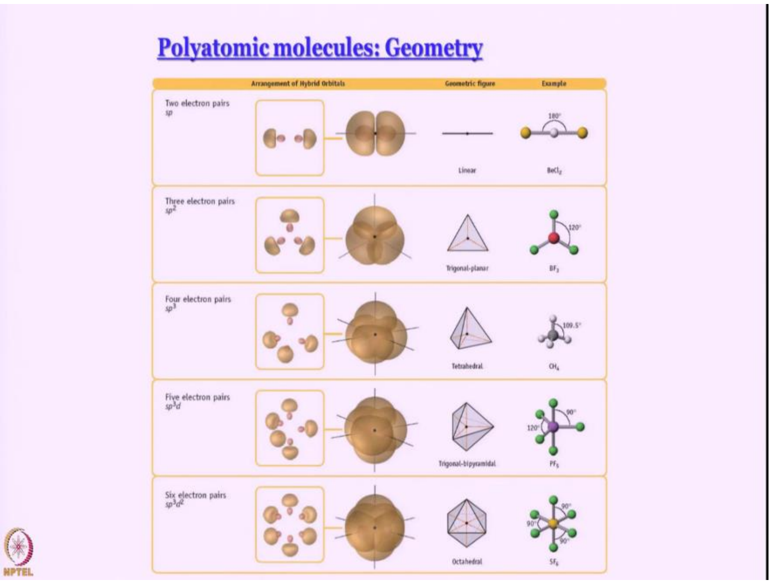

Polyatomic molecules: Geometry

Arrangement of Hybrid Orbitals	Geometric figure	Example
Two electron pairs sp	Linear	$BeCl_2$
Three electron pairs sp^2	Trigonal-planar	BF_3
Four electron pairs sp^3	Tetrahedral	CH_4
Five electron pairs sp^3d	Trigonal-bipyramidal	PF_5
Six electron pairs sp^3d^2	Octahedral	SF_6

So, much for homonuclear and heteronuclear diatomic molecules. What about polyatomic molecules? To explain polyatomic molecules, one needs to invoke hybridization. We are not going to do it here. But let me just put up one flag. If we ask you, why is methane tetrahedral? Many of you are going to say it is tetrahedral because it uses sp^3 orbitals that is wrong. It is VSEPR that determines the shape of the molecule, valence shell electron pair repulsion.

There has to be minimum repulsion for a stable molecule. And it just turns out that if you have four bond pairs the most happy situation is when they form a tetrahedron, not a square planar structure. That is what determines the shape. And to rationalize this shape or keeping the shape in mind to build a quantum mechanical description, that is when we invoke hybridization. It is not the cause. So, this is one parting remark I wanted to make before closing this discussion.