Quantum Chemistry of Atoms and Molecules
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Lecture-63
Beyond Homonuclear Diatomic Molecules

Until now we have come a long way but ah in molecular orbital theory we have learnt how to handle only homonuclear diatomics H 2+, H 2, F 2 so on and so forth. But we do not want to stop there. We do not want to talk only about homonuclear diatomic molecules.

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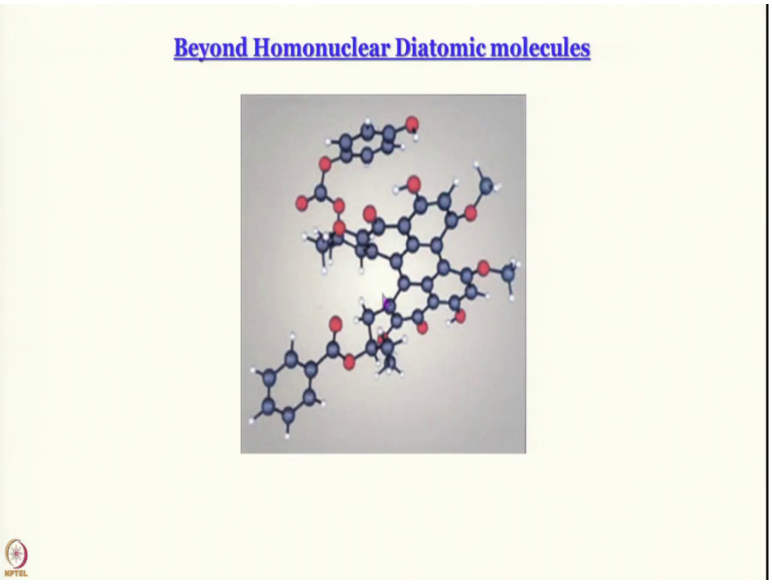

Beyond Homonuclear Diatomic molecules

We want to talk about molecules like these which are neither homonuclear nor diatomic this by the way is calphos in C and what you see here is ah the output of an energy minimized structure calculated using the quantum chemistry calculation software computation software Gamis ah ah it is pretty old now. ah This is from our paper that was published I think in 2000 the work was done in 99. ah The calculation was done to rationalize an experiment that I had performed.

The experiment took a day the calculation took a year using state of the art supercomputer of that time and that is because the molecule is so large. But you can do quantum chemical calculations of molecules that are this large molecules that are neither hormone nuclear nor diatomic and you can get useful results like in this one you can see this red one as usual is oxygen the small white ball is hydrogen. So we see that this OH hydrogen comes perilously close to another oxygen there is a hydrogen bond and then that affects this property of this huge molecule in a very very significant manner.

So of course we will not be able to go all the way where we will know how to calculate how to do quantum chemical calculations for a molecule like this. But let us see first how do we handle diatomic molecules that are not homonuclear heteronuclear diatomic molecules and then let us see how do we handle molecules that are ah not diatomic. How do we handle polyatomic molecules using molecular orbital theory.

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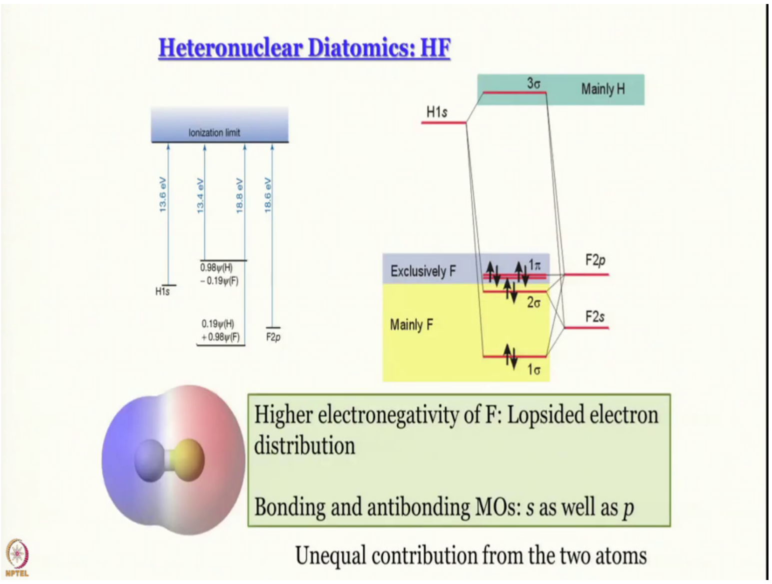

Heteronuclear Diatomics: HF

Higher electronegativity of F: Lopsided electron distribution

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

Unequal contribution from the two atoms

So the first ah heteronuclear diatomic molecule we want to talk about is hydrogen fluoride and here I will take help of some experimental result. The experimental result that I am showing you here is from photo ionization spectroscopy and we will have reason to refer to photo ionization spectroscopy later on in this discussion. What it does essentially is that it measures ionization energy. So what photonization spectroscopy tells us is that ionization potential ionization energy of hydrogen is 13.6 electron volt we already know this number.

For fluorine the smallest ionization energy we get is 16.6 electron fold so that would be from the 2p orbital for HF we get an ionization energy of 13.4 electron volt which is very, very close to the value of 13.6 electron volt for hydrogen and we get another one for 18.8 electron volt which is very, very close to the ionization energy of fluorine 2p. So what we understand from this experimental result is that there is one molecular orbital in HF whose energy is very close to that of 1s orbital of hydrogen and we have another orbital whose energy is very close to that of 2p orbital of fluorine.

So ah when we go ahead and when we do the quantum mechanical treatment we get this expression ah the higher energy orbital expression is 0.98 into ah wave function of 1s orbital of a hydrogen atom plus minus 0.19 psi F and for the lower energy one it is 0.19 psi H plus 0.98 psi F these are not normalized so that the sum of coefficients will be 1. So we have an orbital lower energy that is close to that which is very close in energy and in nature to an orbital of fluorine i.

There is another one that is very close in behavior with an orbital of hydrogen so what we see is that unlike homonuclear diatomics we can have molecular orbitals which have greater contribution from one atom or lesser contribution from one atom. So we can have unequal contribution from the 2 atoms which leads to as we are going to discuss polar covalent bonds. Again from your high school you would have studied about polar covalent bonds and we know many, many examples ah HF, OH in water all these are polar covalent bonds this is how polar covalent bonds show up in an MOT treatment.

And now let me show you the full energy diagram as ah constructed from molecular orbital theory these energies relative energies are more or less they are more or less drawn to scale. So this is the orbital which has energy close to that of hydrogen atom so this is mainly like hydrogen ah 1s orbital. Point to note here is that energy of fluorine is much, much lesser than energy of hydrogen ah sodium orbitals is much, much lesser than the 1s orbital of hydrogen as we have discussed when we talked about homonuclear diatomic molecules of second row.

So the lowest energy1 is mainly fluorine let me go a little further see, what we see here is that we have ah sigma orbitals that are made up of a linear combination of hydrogen 1s orbital fluorine 2p orbital fluorine 2s orbital 2P z has the ah symmetry ah in which it can show overlap as we have discussed earlier. So ah all these 3should contribute to the linear combination but what happens is that the contribution comes from square of coefficients.

Contribution of the fluorine 2s and 2p orbital for these 2 sigma orbitals bonding sigma orbitals is much, much more than the contribution of the hydrogen atom 1s orbital. And similarly for this 3sigma orbital it is still a linear combination of H 1s F 2p F 2s but contribution of F 2p and F 2s is really small compared to that of H 1s so it is a mainly hydrogen atom orbital. Then you have this 2p x and 2p y orbitals of F 2p which ah do not have the symmetry for sigma bonding.

So they are non bonding orbitals on fluorine so we call them exclusively fluorine orbitals. And then how many electrons are there we have 4 pairs we fill them in so we see that the 2 sigma electrons are mainly on fluorine they are on hydrogen also but mainly they behave like their property of ah fluorine atom they are distributed in 2s and 2p orbital of fluorine atom to a small extent in the1s orbital of hydrogen atom.

And what about these 2 pairs these are the lone pairs on fluorine atom remember lone pairs if you just draw ah Lewis dot structure you will see that you get 2 lone pairs and fluorine 2p that is what we get in molecular orbital theory as well the only additional information is that we get to learn that in case of HF these ah lone pair electrons on fluorine reside in pi orbitals. So this is a picture that we get ah since the electron since there is a more contribution of fluorine orbitals.

If you draw the electron distribution or constant probability surface you are going to get something like that dollop sided distribution. In fact its more lopsided than what it appears to be in this cartoon. So unequal contribution from the 2atoms is nicely accounted for in heteronuclear diatomic molecules by molecular orbital theory and what you need to remember is that orbitals must have comparable energy and compatible symmetry so that they can participate in ah linear combination to form the molecular orbitals.

I will say that again ah atomic orbitals must have ah energies that are close by to each other and compatible symmetries, so that they can participate in the linear combination for constructing the molecular orbital. So for HF the linear combination involves H 1s F 2p and F 2s.

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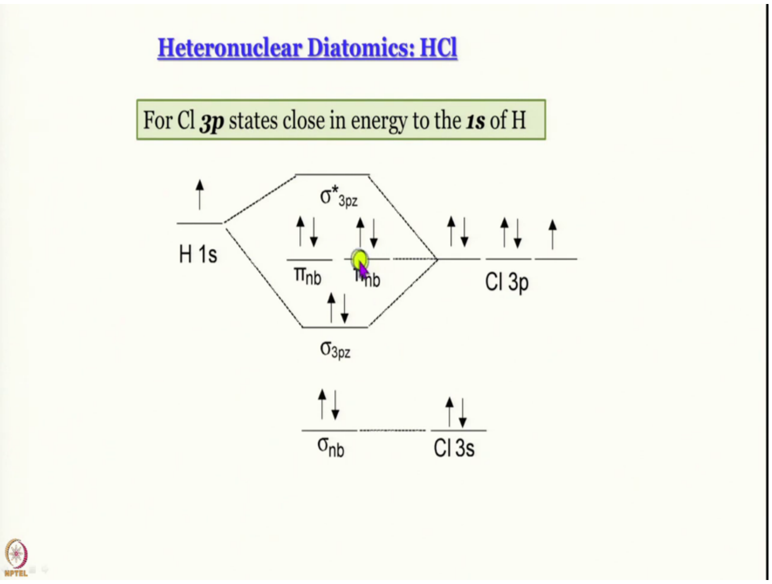

Heteronuclear Diatomics: HCl

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

If you go higher up in the periodic table for HCL well H we have no option it is 1s but for chlorine now the ah 3p and 3s orbitals have energy that is close to H 1s and that is those are the valence orbitals anyway so good thing is you can form this ah linear combination and you can get energy diagram like this.

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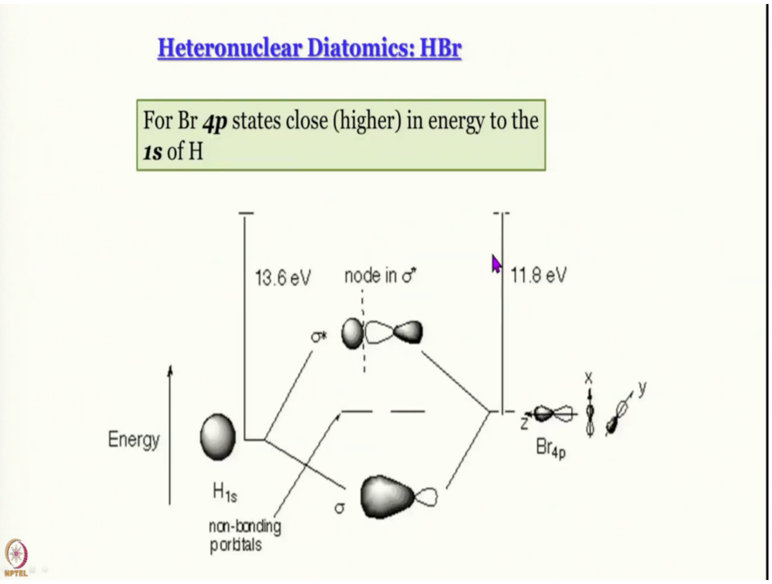

Heteronuclear Diatomics: HBr

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

For bromine now it has become predictable ah we have 4p orbitals that have energy that is close to that of H 1s all these are drawn roughly to scale. And we have shown different things in this diagram for example unfortunately I should have cited the source but I have forgotten where we got it from but what we see is that we also get to draw the MOs this is how the MOs will look you see first of all this ah sigma bonding MO is formed by combining a 1s orbital and a p z orbital there is a node in p z orbital.

So this is what it will look like do not think it is an sp hybrid orbital or anything it is not. It is molecular orbital it is spread over the entire molecule and for the antibonding orbital what will it be I just draw the atomic orbitals in case there is any difficulty in understanding. In this case for the bonding interaction this is your 1s orbital of hydrogen atom and this is the 4p orbital of a chlorine atom and you might remember that actually we are only showing the outermost lobe inside you have shells.

You have plus minus plus that like that but all we are talking about is the major shell ah for further understanding please refer to that lecture where we had drawn these orbitals and we had explained how nodes are and how electron how wave functions are. So this is the bonding combination of atomic orbitals antibonding combination would be if you put plus sign here then it will be minus.

So you will have destructive interference here that is how you get a molecular orbital that looks like this you have constructive interference here that is how you get a molecule orbital that looks like this. But please do not forget that your fluorine atom is here and ah sorry not fluorine what is this bromine, bromine atom is here and hydrogen atom is here. So that is what we get from molecular orbital theory in heteronuclear diatomics we get ah lopsided molecular orbitals and lopsided electron distribution consequently.

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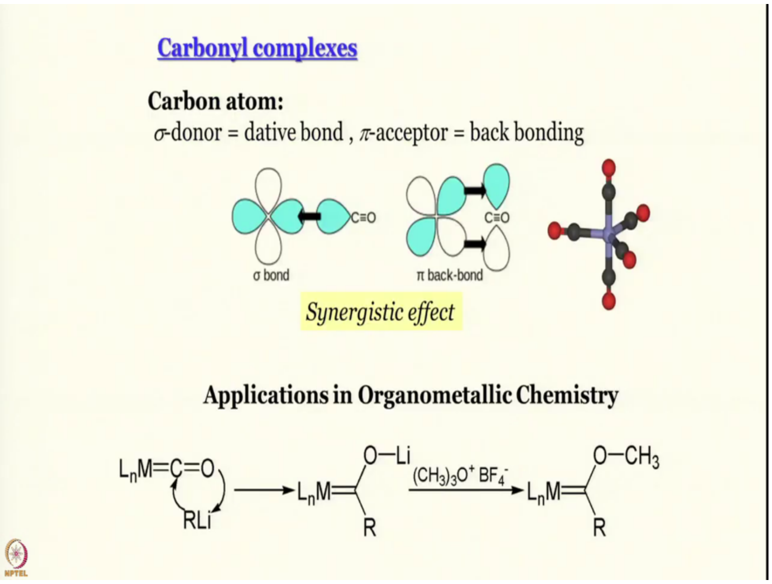

Carbonyl complexes

Carbon atom:

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

Synergistic effect

Applications in Organometallic Chemistry

Now we want to talk about carbonyl complexes so carbonyl CO carbon monoxide is a very, very important molecule from the point of view of chemistry as well as physiology. It is known that carbon monoxide forms ah carbon monoxide uses this carbon atom as a good sigma donor in formation of coordinate bonds and also it can accept pi electrons or MTD orbitals we say. Well maybe the orbitals or what is it you know sorry I goofed up a little bit there.

This d orbital is that of the metal from there ah electron density can actually come back and be accommodated in some orbital of carbon monoxide we will see which are vital so back bonding is there. This is called synergistic effect in inorganic chemistry so that is why carbonyl ah well carbon monoxide can form very stable strong carbonyl complexes. And this complexes has applications in organometallic chemistry like the one that is shown here you take a molecule like this a complex like this.

Oxygen atom lone pair can attack say butyl lithium and then this R group butyl group in butyl lithium that gets attached to carbon. Once again carbon here is accepting electron pair and then whatever happen, happens. So the question is why is it that carbon can act as a very good sigma donor and then how is it that it can act as a good pi acceptor also.

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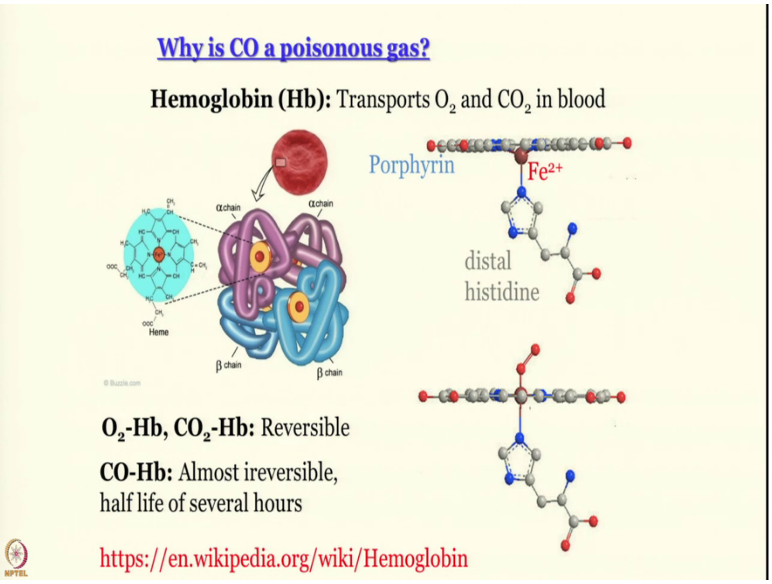

Why is CO a poisonous gas?

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

To answer this question ah we construct a molecular orbital picture but before that let me also state that carbon monoxide is important physiological as well because you might know carbon monoxide is a highly poisonous gas. As highly poisonous gas because it goes and attaches with hemoglobin, hemoglobin as we know is a carrier protein it transports oxygen and Co 2 in blood and the way it does it is that this here is the structure it is a ah tetramer and it is a metal of protein?

It has Fe 2 plus and ah there is a ligand which is sort of like profile in him and ah then ah this is what happens. In the heme center initially you have a low spin complex so this Fe 2 plus actually hovers above the ring and the 5th position is taken up by a distal histidine. Now when from the other side oxygen or Co 2 ah comes and coordinates then it transforms to a low spin complex size becomes smaller and this Fe 2 plus goes and fits nicely in the cavity of peripheral.

So that is how it takes up oxygen that is how it takes up carbon dioxide and it can give up oxygen and carbon dioxide easily wherever required that is because these oxyhemoglobin and carboxy hemoglobin that is this complexes that are formed they are formed reversibly. The problem is carbonyl well carbon monoxide forms carbonyl complexes that are extremely stable the formation is almost irreversible.

So once that complex is formed half life is of several hours. So if ah somebody is exposed to carbon monoxide all these or a lot of these hemoglobin molecules will form this very, very stable carbonyl complex with carbon monoxide which is not going to break. So easily so they will not be able to participate in oxygen and carbon dioxide transport that is most important for life processes.

So the question is why does carbon monoxide form such a good complex why is it that it can be a good ah sigma donor from carbon and why can the same carbon atom be a good pi acceptor. ah

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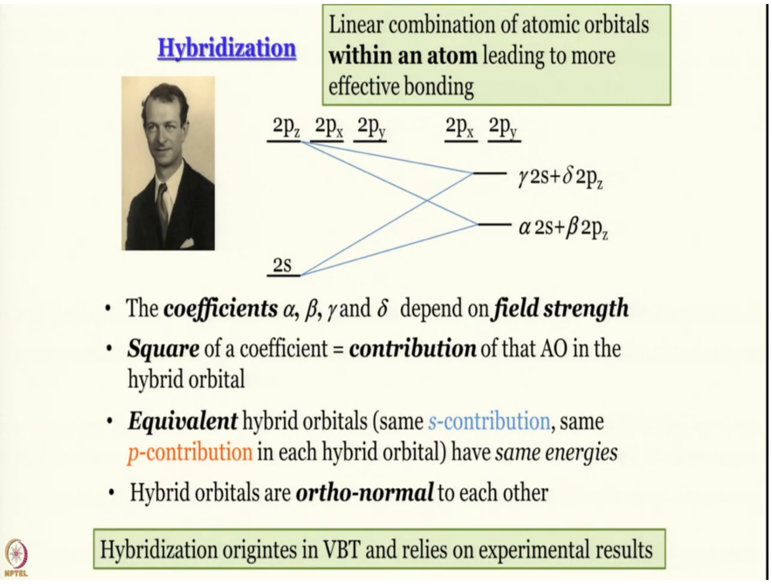

Hybridization

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

The somewhat contentious ah molecular orbital picture that has been constructed to explain this involves this concept of hybridization that we have discussed already. And here one thing I want to remind you is that it is not necessary that all hybrid orbitals have to be equivalent they can actually have different energies it depends on what alpha beta gamma delta coefficients are.

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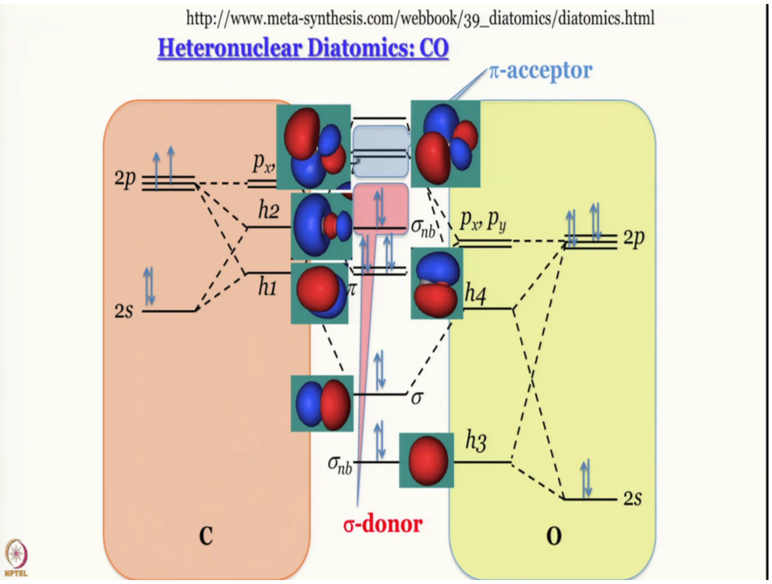

http://www.meta-synthesis.com/webbook/39_diatomics/diatomics.html

Heteronuclear Diatomics: CO

Now with that background this is the contentious model I was talking about. These are the ah 2s and 2p orbitals of carbon once again more or less drawn to scale as far as energy is concerned these are the 2s and 2 orbitals of oxygen. So in the model that is used remember ah we know the result already to explain it we are constructing a model working out the energies and trying to see whether it makes sense.

It might make sense to a certain extent and then it might not we will see. So the model involves hybridization forming formation of 2 hybrid orbitals non equivalent hybrid orbitals of 2 different energies for carbon as well as for oxygen. So for carbon H 1 is a lower energy hybrid orbital let us say H 2 is a higher energy hybrid orbital. Now hybridization here we are talking about sigma bonds. So ah hybrid orbitals accommodate ah sigma bonds they are used for sigma bonding.

So ah the p orbital that participates in this hybridization would be p z if we take z to be the direction of approach of the 2 nuclei. So p x and p y do not have the ah symmetry as we have discussed earlier so they remain non bonding orbitals on carbon. Now well should not even say non bonding now they remain ah in a pure unhybridized form on carbon. Similarly in oxygen you invoke hybridization form H 3 and H 4 and p x and p y remain as such.

So now this p x and p y are actually available for pi bonding will come to that. Now here in there is an objection why do we have to use H 3 and H 4 for oxygen. If you go back to homo nuclear diatomics we said that this ah mixing of 2 orbital does not even take place for oxygen. So why would it take place here? So one argument is that the C o is ah isoelectronic with n 2 if you compare nitrogen ah oxygen has one electron more carbon has one electron less so here even the oxygen atom should behave like carbon atom that is the sort of the argument that is used.

So now let us try and see ah which orbitals have comparable energy and appropriate geometry. Do you think H 3 will participate in formation of sigma bond? This is the energy of H 3 this is you know energy increases as you go up H 3 has very low energy compared to H 1 and H 2. So it is going to remain non bonding. Similarly H 2 has a little high energy compared to H 4 so it will remain non bonding the difference is H 3 remains non bonding on oxygen H 2 remains non bonding on carbon.

What about H 1 and H 4 their energies are close enough so they form a linear combination to give you the bonding sigma orbital and antibonding sigma star orbital. What about p x and p y now p x and p y are like this these are x orbitals these are y orbitals they can form a pair of pi bonds. So you can generate 2 sets of degenerate pi orbitals and pi star orbitals also. So ah when I write degenerate is important to understand what I am really saying is this I do not think I talked about this earlier.

So I can write like this I will call it pi x is equal to C 1 p x of carbon plus C 2p x of oxygen phi y will be C 3 p x of carbon plus C 4 p x of oxygen. And similarly when you take the antibonding combinations you will have minus instead of plus here and the coefficients are going to change. So, here also symmetry becomes important see p x and p x let us say this is x axis now. They are in the orientation they are the symmetry to participate in a pi kind of linear combination.

But this p x and that p y do not the 2p y orbitals can participate in linear combination. So while constructing this pi MOs we do not take p x C plus p x ah O plus p y C plus p y O we do not do that we only take x's and y's so this is how the problem of formulation becomes a little simpler. Now we have to fill in the electrons, how many electrons does carbon have 2 3 4, 2 pairs and what about oxygen 2 4 6, 3 pairs.

So now we have ah 6 + 4; 10 electrons will start filling them up in pairs so sigma nb the lowest one H 3 is going to have a pair sigma ah from H 1 and H 4 will have another pair and we have 4 electrons more they will reside in the pi orbitals, pi molecular orbitals is there anything more? Yes 1 pair in sigma n b remember sigma nb is a non bonding orbital that is a an exclusive property if you want to call it that of carbon atom.

It is localized on carbon atom so what we see is that this and sigma, sigma means it is going to be highly directional. Now let me tell you the reason why this hybridization was done is that this is known to be used well this is what we think participates in sigma donation. So if you want sigma donation to take place you want a highly directional orbital hybrid orbitals are more directional than your p orbitals.

So that is why ah this hybridization was used in the first place. So, now this model nicely explains why CO can act as a good sigma donor through the carbon atom because the highest occupied molecular orbital is a non bonding orbital localized on carbon. And why is it that it can accept electrons and remember the diagram I had shown you earlier. When we talk about synergistic effect when we talk about back bonding then this is the diagram I had shown and I had goofed up a little bit.

This here is a d orbital of the metal ion, we drew an orbital on the same carbon of carbonyl like this, this has to be an empty vacant orbital and we said this is how the electron cloud gets transferred. So this d orbital is filled and the whatever this orbital is, is vacant. Now remember this is the sigma bond. So any orbital that is perpendicular to the sigma bonding orbital what kind of orbital would it be?

It has to be a pi orbital and I will show you in a minute what these pi star orbitals look like. So what we see here is that carbon also has this low lying vacant pi star orbitals which have the symmetry which enables it to accept any electron cloud that comes back from the ah central metal atom the orbital. So this is the orbital that is used in the action of carbon atom to behave like pi acceptor in carbonyl complexes.

Now let me show you the orbitals molecular orbitals and again this is a little contentious. ah What I would like to you to focus on is this sigma and v orbital see it is on carbon heavily on carbon and pointed towards one side it looks like hybrid orbital and this is the pi star orbital again it is close to the carbon orbitals carbon p x orbitals. Look at the bonding ones the bonding ones are close to that of oxygen pure p x b y orbitals.

The anti bonding ones are actually lopsided towards carbon because they have a greater contribution from p x and p y orbitals of ah your carbon atom that this is the model that can nicely rationalize ah why ah carbon monoxide is such a good ligand why it forms good sigma bonds to carbon atom and why the same carbon atom can efficiently accommodate electron cloud coming back from the central metal atom. That brings us to an end of our discussion of ah heteronuclear diatomic molecules.

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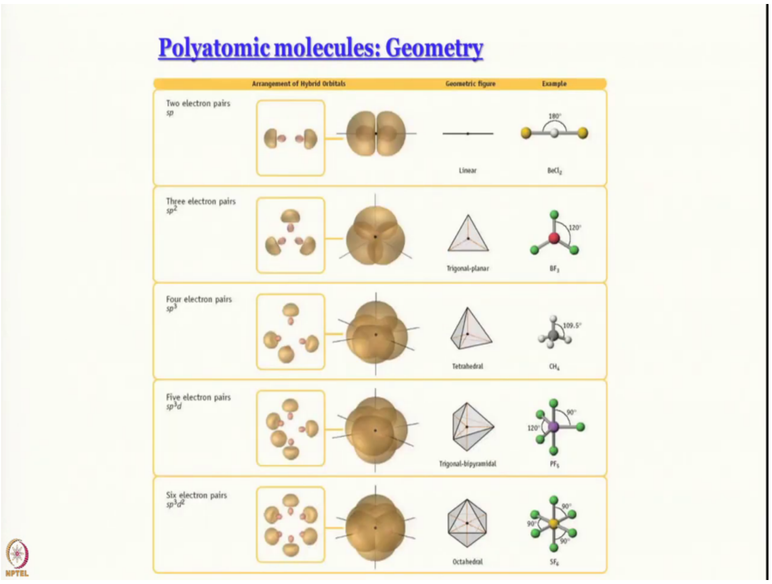

Polyatomic molecules: Geometry

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

In the next class we are going to go back to polyatomic molecules but this time we are going to learn how one can use molecular orbital theory to understand ah polyatomic molecules.