Quantum Chemistry of Atoms and Molecules
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-64
MOT for Polyatomic Molecules

We are slowly getting towards the climax of our course. We have talked about homonuclear diatomic heteronuclear dy namics. We have discussed how MOT can nicely explain why carbon monoxide behaves as a strong sigma donor through carbon atom and a good pi acceptor through the same carbon atom. Now what we want to do is we want to venture into poly atomic molecules. So today and for the rest of this course we are going to discuss molecular orbital theory for poly atomic molecules.

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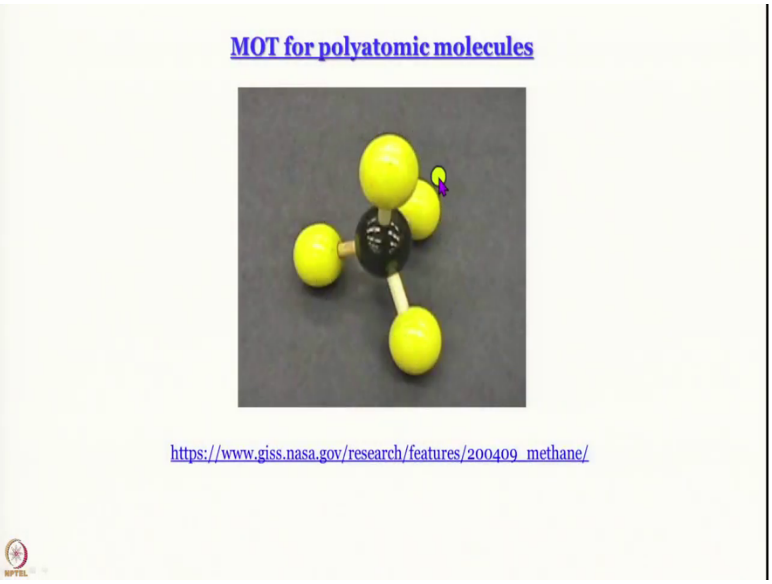

MOT for polyatomic molecules

https://www.giss.nasa.gov/research/features/200409_methane/

And today we will discuss the case of only 1 molecule the favorite molecule of all chemists methane very nice tetrahedral molecule. We have already discussed the valence bond approach towards understanding a molecule like this. Let us see how different MOT is does it give us the same result does it give us some new information what happens?

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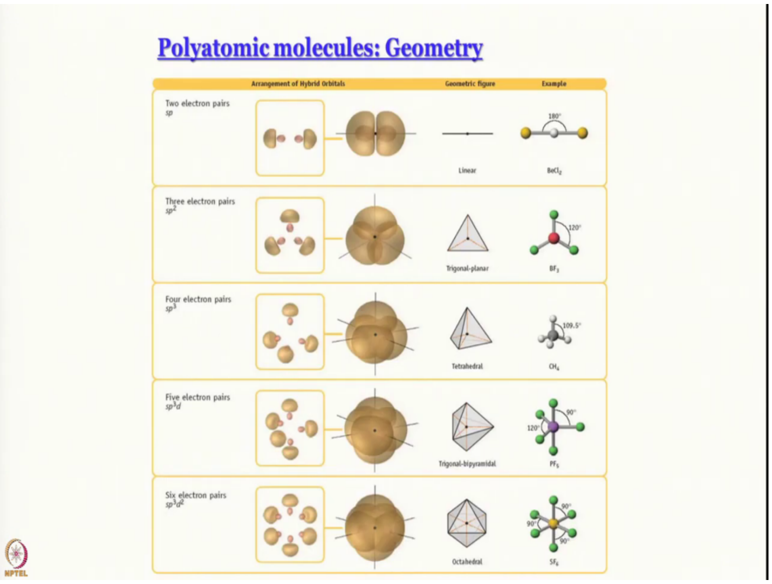

Polyatomic molecules: Geometry

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 the motivation for doing this of course is that poly atomic molecules have a particular kind of geometry and this geometry is explained very nicely in valence bond theory by the use of hybrid orbitals. Now it is not as if you cannot set up molecular orbital theory for polyatomic molecules using hybrid orbitals 1 might be tempted to do so because then the geometry is retained. The problem is hybrid orbitals are associated with localization.

If you remember what we had discussed for carbon monoxide the whole reason why hybridization of carbon atom orbitals was invoked was that we would get very highly directional sigma hybrid orbitals H 1 or H 2 whatever we call it at that time. So if you use hybridization if you use hybrid orbitals and you construct MO picture then you would get a an MO picture where electron clouds would be strongly localized.

But then that gives up the biggest advantage molecular orbital theory has over valence bond theory and that advantage is that of delocalization. What I am trying to say is this suppose we are talking about methane I will draw that box as usual how do we draw it I do not remember exactly how I have drawn it later on but I will just write like this. Put 1 dot here leave aside the next 2vertices put another dot in the next again leave aside the other vertices.

So where will I go I will go here and here so of course these are the 1s orbitals. Let us say p q r s these are hydrogen atoms or we can say that they are the 1s orbitals what do I do where is carbon atom at the body center somewhere here. So I can take an sp 3 hybrid orbital here say pointing towards p then when I draw the MO I will call it psi p that will be some C 1 multiplied by psi 1s of p plus C 2 of H 1 I will call this H 1.

Similarly you can write psi q will be equal to some C 3 into psi 1s of q plus C 4 into H 2 where H 2 would be the hybrid orbital pointing towards your cube. So this way I can write 4 molecular orbitals that would be the localized MOT for methane. If there is a case what kind of energy diagram would I get sorry I should have actually made a slide where I had I would have shown all this for whatever reason I forgot.

But let me please bear with me this is the we can draw this energy diagram without much fast. Let us say this is your carbon 2s and 2p and we have generated 4 equivalent sp 3 hybrid orbitals. So that is 3, 4 and let us say hydrogen atom 1s wave function has energy somewhere here. So what I am saying is if this is the case I should draw 4, 1 2 3 4 because there are 4 hydrogen atoms p q r s. So the simple localized MOT would give me a picture like this. I have 4 degenerate molecular orbitals well 4 degenerate bonding molecular orbitals 4 degenerate anti bonding or molecular orbitals.

The bonding ones would be all doubly occupied and if this is the case if I look at ionization energy out, if I look at ionization energy what kind of ionization energy should I get, only 1 value of ionization energy. So now let me talk a little bit about photo ionization photoelectron spectrum. What is photoelectron spectrum? You give so much of energy is x-ray typically or sometimes very high energy UV light that an electron comes out and goes into the continuum.

Electron gets detached the molecule gets ionized so typically what you do is you use very high fixed value of energy let us say 20 electron volt. And let us say kinetic energy sorry let us say ionization energy of the orbital from which this is removed let us say that is sorry 13 electron volt. So kinetic energy of the electron is going to be 7 electron volt 20 – 13, simple. Let us say this some other energy level at 11 electron volt then kinetic energy will be something like 20 – 11, 9 electron volt.

So if I plot something like intensity against kinetic energy of electron or I can just write ionization energy I should get 1 band single band in photoelectron spectrum is what is predicted from localized molecular orbital theory which is nicely in accordance with our valence bond picture. However as I said this gives up on the biggest advantage and that biggest advantage is your delocalization. So what we will do is we will talk about delocalized mot but before that I request you please remember this discussion.

If I use localized molecular orbital theory then I am going to get 1 value of ionization energy 1 band in the photon photo electron spectrum that being said.

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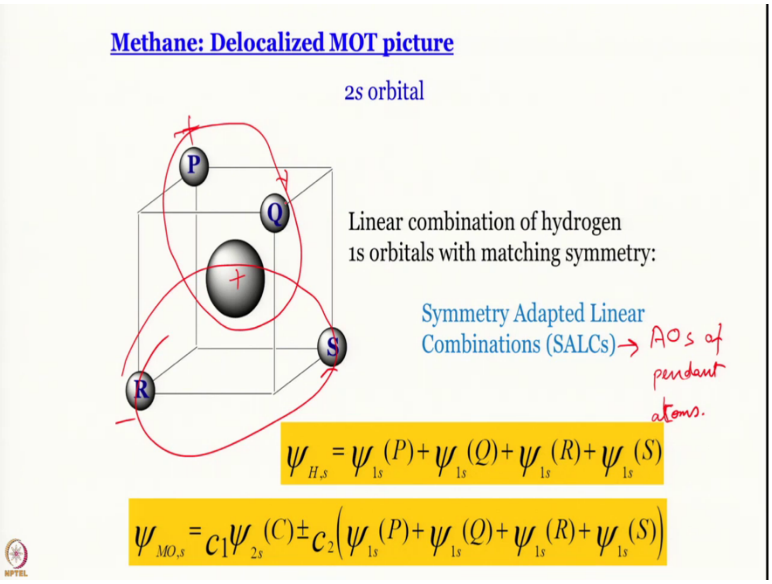

Methane: Delocalized MOT picture

$2s$ orbital

Linear combination of hydrogen 1s orbitals with matching symmetry:

Symmetry Adapted Linear Combinations (SALCs) → AOs of pendant atoms.

$$\psi_{H,s} = \psi_{1s}(P) + \psi_{1s}(Q) + \psi_{1s}(R) + \psi_{1s}(S)$$

$$\psi_{MO,s} = c_1\psi_{2s}(C) \pm c_2\left(\psi_{1s}(P) + \psi_{1s}(Q) + \psi_{1s}(R) + \psi_{1s}(S)\right)$$

Let us go ahead and discuss delocalized molecular orbital theory picture what does that mean I want delocalization. So I not use hybrid orbital and will remember that atomic orbitals with proper symmetry can only be combined. So now see carbon atom central carbon atom has 2 orbitals that are relevant in our discussion 2s and 2p and this 2s and 2p can separately form linear combinations of hydrogen 1s orbitals with matching symmetry.

So what we do is we first construct a linear combination of p q r and s 1s orbitals and we make combinations of particular symmetries that is why these are called symmetry adapted linear combinations SALC's in short or SALC. If I am speaking Hebrew and Latin now please bear with me for a few more minutes things will fall in that place. But remember symmetry adapted linear combinations are constructed using the atomic orbitals of the pendant atoms.

Carbon a central atom and this hydrogen atoms are sort of hanging or are suspended from carbon they are called the pendant atoms. You have to perform symmetry adapted linear combinations linear combinations of pendant atom wave functions orbitals that have the matching symmetry with 2s orbital and then later on to pure vitamin what would the matching symmetry be. In this case if we take p plus q plus r plus s I am calling it psi H s psi 1s of p plus psi 1s of q plus psi 1s of r plus psi 1s of s that has matching symmetry is not it.

So if I take linear combinations like this C 1 multiplied by psi 2s plus minus C 2 multiplied by this psi H s what do I get when the sign is plus then I get bonding orbital bonding molecular orbital when the sign is minus then what happens this one is plus sorry this one is plus let us say I have plus here plus here minus here minus here then for this part of the MO you are going to get bonding for this part of the MO you are going to get antibonding.

So it is a non bonding situation or if 1 is plus 3 or minus same thing will happen. So I hope now you understand what the meaning of symmetry matching is. Symmetry of the linear combination of atomic orbitals or symmetry of these SALCs have to be the same as the symmetry of the orbital atomic orbital of the central atom. So for 2s orbital the SALC that has comparable symmetry is just plus plus plus plus psi 1s p plus psi 1s q plus psi 1s r plus psi 1s s.

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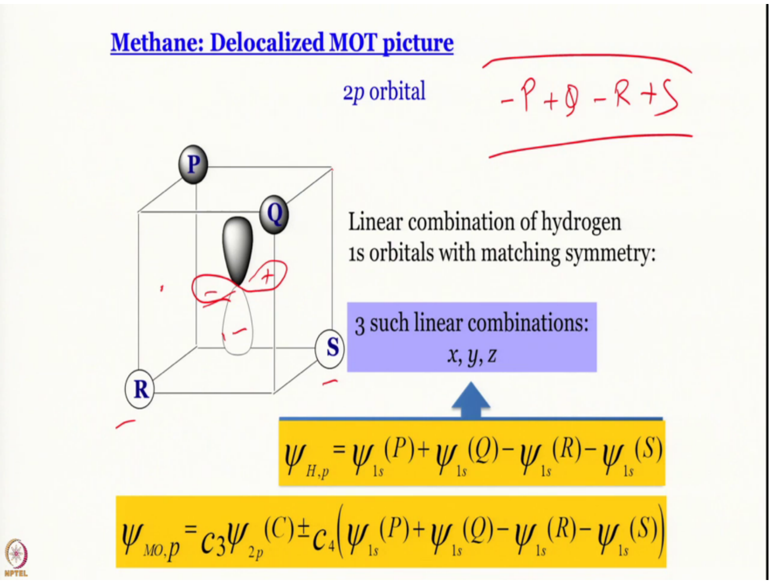

Methane: Delocalized MOT picture

2*p* orbital

$-P+Q-R+S$

Linear combination of hydrogen 1s orbitals with matching symmetry:

3 such linear combinations: *x*, *y*, *z*

$$\psi_{H,p} = \psi_{1s}(P)+\psi_{1s}(Q)-\psi_{1s}(R)-\psi_{1s}(S)$$

$$\psi_{MO,p} = c_3\psi_{2p}(C) \pm c_4\left(\psi_{1s}(P)+\psi_{1s}(Q)-\psi_{1s}(R)-\psi_{1s}(S)\right)$$

What about p orbital, which linear combination of hydrogen orbitals will have matching symmetry with p orbital remember here this slope is plus and this slope is minus sine of wave function. So if I want to have matching symmetry then p should be plus q should be plus r should be minus s should be minus is not it yeah that is what I have shown here fill circles means plus and empty circles means minus.

This has matching symmetry, so if I take a plus combination between these 2i get bonding if I take minus combination then I get antibonding. We will call this H psi H p is psi 1 s plus psi 1 s well psi 1 is p plus I minus q minus psi 1 is r minus I 1 is s you can now take linear combinations see what has happened I am constructing molecular orbitals by taking linear combinations of a lesser number of central atom wave functions.

I do not have to take 2s and 2p together I take either 2s or 2p and depending on which atomic orbital I take of the central atom I will choose a linear combination of compatible symmetry of the pendant atom orbitals symmetry becomes very, very important that is point number 1. So how is it that symmetry of 2s and 2p are different well 2s has no node and this one has a node. So if you think of inversion for example this will be anti-symmetric with respect to inversion whereas your 2s will be symmetric with respect to actually everything.

So 2s orbital is totally symmetric meaning no matter which symmetry operation you use its sign does not change it remains the same. Whereas by using some symmetry operations well there is no center of inversion actually in case of a tetrahedron but we do have C 2's. So now think of this C 2 turn by 180 degrees what happens this goes here that goes here. So this becomes negative, so what I am seeing is that this orbital here is anti symmetric with respect to C 2 this another C 2 here it is anti symmetric with that C 2 also.

However with respect to this C 2 it is symmetric. Similarly you can think of the of the planes this for example is a plane but I will show this plane this is better is this a plane, plane of symmetry? Yes it is, might as well it is the other one just to ensure that I do not confuse you there is everything else actually you see the plane. So with respect to this plane what happens to this linear combination p q r s q goes to s and p and r remain in the same position.

So it changes, so there will be symmetry operations which will change the sign of this linear combination. So it will be symmetric with respect to sum it will be anti symmetric with respect to sum. So behavior in response to symmetry operations is not the same for 2s and 2p orbitals they have different symmetries point number 1. Point number 2 I have only drawn let us say the p z orbital. If I draw p x for example if I drop p x like this let us say this is x then which linear combination of pendant atom wave functions will have matching symmetry?

It will be well this is plus that is minus so p and r have to be have negative coefficients q and s have to have positive coefficients so that will be minus p plus q minus r plus s this kind of linear combination will be required. Similarly you can work out what it will be for p z. Now all these linear combinations are different from each other but they have the same symmetry p x p y p z they are in different orientations they are the same symmetry.

So we have 2 kinds of molecular orbitals now one arising out of 2s other involving 2p 2 kinds of molecular orbitals.

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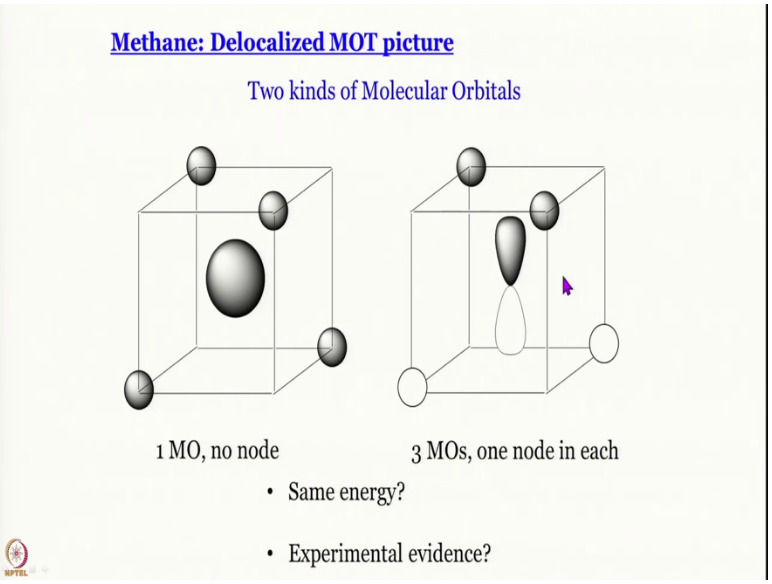

Methane: Delocalized MOT picture

Two kinds of Molecular Orbitals

1 MO, no node

3 MOs, one node in each

- Same energy?
- Experimental evidence?

These and these they have different symmetries and remember this kind of orbitals is 3 fold there are 3 MOs of the same symmetry will they have the same energy? Actually no, because there is no node here there is a node here. So what we expect now is that we should have 2 groups of molecular orbitals very different from what we were expecting from localized MOT treatment. We now expect that there will be 2 groups of molecular orbital there will be a group of one arising out of 2s.

There will be a group of 3 involving the p x p y p z orbitals of the central carbon atom. Will they have same energy? No because remember more nodes translates into more energy.

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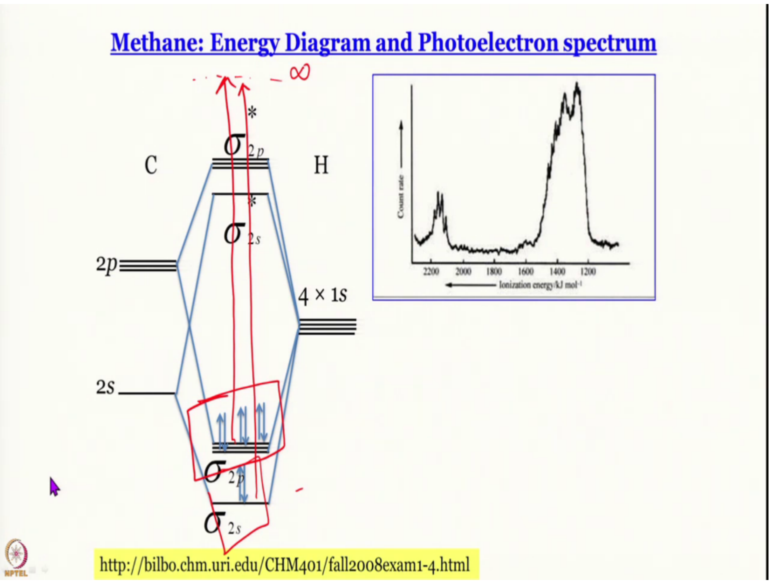

Methane: Energy Diagram and Photoelectron spectrum

http://bilbo.chm.uri.edu/CHM401/fall2008exam1-4.html

So, now we have this interesting situation this one I have drawn so I do not have to draw by hand we have 2s orbital and 2p orbitals of carbon atom we have 4 1s orbitals of hydrogen atom they combine but this time we do not hybridize the carbon atom orbitals rather we take an appropriate linear combinations we have 4 linear combinations from here also p plus q plus r plus s p minus q minus r minus s p plus q minus r minus s and I have forgotten what I said so you work out what the 4th 1 will be.

So, I get 4 degenerate SALCs here instead of the 4 1s orbitals. So the first 1 gives me the sigma bonding molecular orbital with 2s that we call it sigma 2s correspondingly there will be an antibonding sigma 2 star orbital and there will be 3 degenerate 2p orbitals 3 degenerate 2p star orbitals different picture is obtained from delocalized MOT approach to methane from what we got from the localized MOT approach. First let us fill in the electrons 2 4 6 8. How many ionization energies will be there? 2.

So I should have 2 kinds of ionization energy because ionization energy means let us see if I can draw a straight line now. Let us say this is the continuum this will be one ionization energy this will be another ionization energy which is more obviously this. So, sigma 2s orbital is associated with an ionization energy that is greater than ionization energy of sigma 2p point number 1. Point number 2 is that the population of sigma 2p is thrice that of population of sigma 2s.

So in photoelectron spectrum the band corresponding to sigma 2p which means the lower energy lower ionization energy band that should be 3 times as intense as the band arising from sigma 2s that is the higher ionization energy band. Now is a moment of truth I will show you the photoelectron spectrum and you can judge for yourself which picture is correct, localized MOT picture where we expect 1 kind of ionization energy or delocalized MOT picture where we expect first of all 2 kinds of ionization energies.

And secondly the band corresponding to the lower ionization energy should be 3 times strong as that of the higher ionization energy. The answer to that; remember Max Planck experimental results are the only truth; here is the truth. You see lower ionization energy has a larger band higher ionization energy has a lower band, well even before the saying that I should have said that there are 2 bands meaning 2 ionization energies.

So the delocalized MOT picture gives me the correct result localized MOT picture does not. I would better erase this so that it does not cover up what I have written later that would be enough. So we do have 2 kinds of MO's 2 kinds of energy levels and that should disturb us what is the meaning of 2 kinds of MO's I mean the bonds are all equivalent otherwise how is it a tetrahedron bond lengths are all the same.

So is that a contradiction is there a conflict between this delocalized MOT that gives us 2 different kinds of MO's and our knowledge that the 4 bond lengths are equal. Actually there is no contradiction, it is important to remember that MO’s are not bonds. MO’s tell you about the wave function and in delocalized molecular orbitals every wave function is delocalized over the entire molecule go back and have a look at the wave functions.

Each of the wave functions no matter whether its sigma 2s or sigma 2p is delocalized over all the 4 hydrogen atoms and the carbon atom. Bond by definition refers to the electron density between 2 given atoms carbon atom and a particular hydrogen atom. So what happens is that each of these MO’s contributes equally to each bond because they are distributed homogeneously. So every MO contributes the same amount to the electron density buildup between a given pair of carbon and hydrogen atoms.

Well between carbon and a given hydrogen atom. So this is an important thing to understand MO and bond are not equivalent to each other. They are interrelated but they are not equivalent. So there is no contradiction whatever we get from valence bond picture equal bonds is what we can rationalize by MO picture as well. And this is a good example of a very fundamental quantum mechanical principle that we had stated towards the beginning of our class.

Properties of the system that you see depends on the experiment you perform. Eigen value that you get depends on which operator you apply take the same psi make Hamiltonian operate on it, it will give you energy make p x operate on it, it will give you linear momentum along x.

Similarly the experimental equivalent of using operators is to use different techniques. You do photo ionization spectroscopy then you probe the actual energy levels the MO's photoionization energy gives you a knowledge of MO's.

So you get to see the MO's you do rotational spectroscopy or you do extra crystallography if possible not about methane then you get an idea about the bond lengths. So this is very much like the proverbial blind man trying to figure out what an elephant looks like. The one who touches the foot says the elephant looks like a pillar the one who touches the trunk says the elephant looks like a horse pipe.

The one who touches the tusk says the elephant looks like a pointed sword pointed downward soul or a sphere. Elephant does not look like any of these the holistic picture of the elephant is a linear sum of everything. So you perform a different experiment you get to see different property like this proverbial blind man sampling different body parts of the elephant. This is an important take home message that is sort of a side product of our discussion of molecular orbital theory for methane.

So we have learnt something very important we have learnt that it is better to use delocalized molecular orbital theory when we are talking about when we talk about poly atomic molecules and we get to understand that we can actually figure out which of our theoretical models is correct by comparing with experimental results. Even then you can go wrong remember both theory gave us the correct value of rydbergconstant still we had to discard it.

But at least your theory should match some experimental observation. So that is what we wanted to say about methane. So we are done with discussing sigma bonds now we go on to the last part of our discussion that is for pi bonds pi molecular systems. And that is where we will see that we use another kind of approximation called Huckel approximation that is what we are going to learn in the next 2 or 3 classes and that will take us to the end of this course.