eQuantum Chemistry of Atoms and Molecules

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Lecture-57

Molecular Shape and Hybrid Orbitals

So, far we have discussed ah diatomic molecules. Now let us expand the scope of our discussion a little bit and now we want to talk about ah not necessarily diatomic not necessarily linear molecules we want to talk about little bigger molecules and while doing that ah we know that molecules have their own characteristic shape. So, this is something that we have studied ah Gillespie and Nine homes approach of valence shell electron pair repulsion theory.

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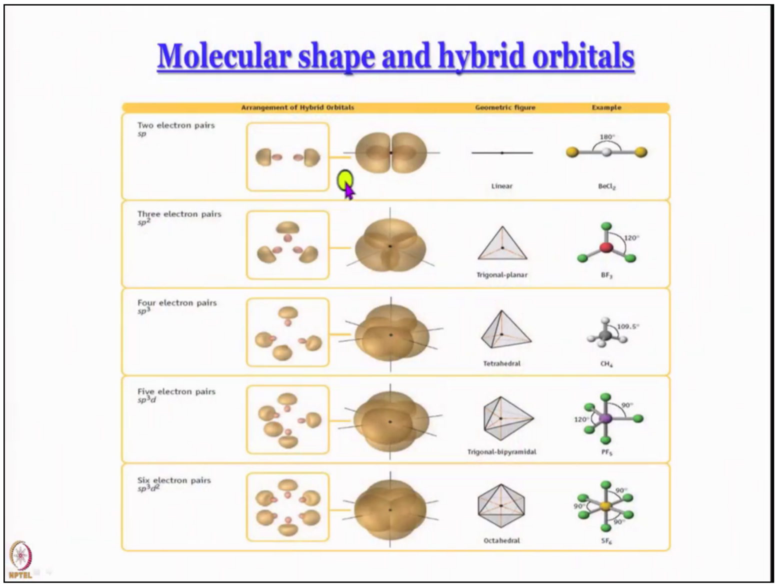


Molecular shape and hybrid orbitals

	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

There we know that we have an AB 2 kind of molecule then it is going to be linear if it is AB 3 where A is 1 atom central atom and ah B is another atom you can say pendant atom then we will get a trigonal planar molecule AB 4 tetrahedral AB 5 trigonal biplaner trigonal bipyramid sorry AB 6 octahedral of course these are all regular solids regular molecules and these are all molecules in which you have a central atom holds very nicely for metal complexes for example.

And the reason why molecules have these shapes please remember because very often by mistake we put the card before the horse. The reason why molecules have this shape is valence shell electron pair repulsion has to be minimized. So, if you have a situation in which you have 2 bonds this is one, this is another bond then ah if they are like this and suppose there is no other lone pair or anything there will be some repulsion then what will happen they will try to open out open out open out when they are at 180 degrees to each other then this repulsion between what we can call bond pair of electrons is minimum.

That is why AB 2 so 2 bonds means what have central A atom AB atom here and B atom here this AB 2 is going to be a linear molecule what happens if I have a trigonal planar molecule unfortunately I do not have a third pen so I will just use this. So trigonal planar again you have say 3 bonds you put them at some angle something like this or you take a pyramid then you repel repel, repel, repel and finally if these bonds are all equal if it remember we are talking about AB 3 kind of molecules which means all the ah bond pairs are ah equivalent.

Then the repulsion will be minimum when they are all in a plane and the angle between 2 is 120 degrees. So generally when I go to class I do something which I have not been able to do today because well what I do in class is I take balloons I blow up balloons and I tie them up and I show that when you tie up 2 balloons hold like this you will always get a straight line 2 balloons like this then if I try 2 more balloons and wrap them together in front of your eyes you get a tetrahedron yeah balloons are balloons there no hybridization or nothing.

So ah what holds for balloons also holds for electron clouds in air in the balloon that wants to stay in a comfortable manner similarly electron clouds want to stay in a comfortable manner. So it is important to understand that VSAPR is essentially a steric effect. Lone pairs occupy more volume because they are not bound at 1 end. So lone pair bond pair repulsion lone pair repulsion is maximum lone pair bond pair repulsion follows bond pair bond repulsion is minimum but whatever repulsion it is you want to minimize it and that is why the molecules take up whatever shape they take up.

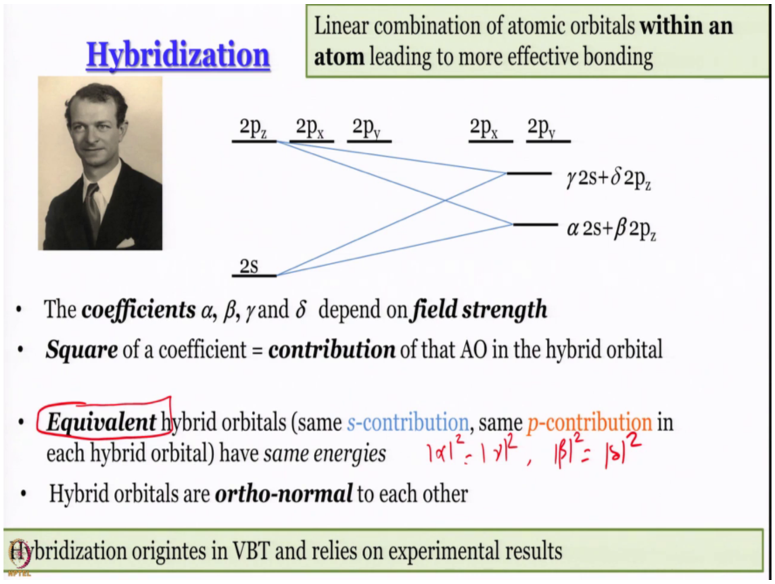
So unfortunately ah now we are in lockdown and I do not know where to buy balloons and then I have to blow all of them up by myself I do not have anybody to help so you do it yourself. Please blow up balloons you might have seen it in parties and all when they tie up balloons they always tie in pairs and then they roll them together and what with the shape you get is a tetrahedron. Why do you get a tetrahedron? Because a tetrahedron is the minimum ah bond pair bond pair repulsion geometry for an AB 4 kind of molecule.

Similarly if you roll 2 more balloons there you will get an octahedron and so on and so forth. You watch 1 of the balloons in octahedron it will become trigonal bi pyramid TBP in front of your eyes unfortunately I cannot show that to you now but I encourage you to please do the experiment yourself and see is a lot of fun you can demonstrate it to even it is 5 year old kid and they will be amazed and they will be amused and impressed and well it amuses me every time I do it so I hope it will amuse you as well.

So this is the crux of the matter molecules have certain shapes because of VSEPR they want to minimize the ah lone pair lone pair lone pair bond pair bond pair bond pair repulsions. The problem is this if I want to build say a valence bond description of such a molecule how do I do it? Because I have to use orbitals that are there in the atoms, atoms that consider the molecules how do I do it? Because for example I want to make I want to talk about this AB 3 kind of molecule BF 3 let us say boron has 2 s orbital and 2p orbital.

It does not have orbitals ah which have angles of 120 degrees between each other so what do I do? What I do is that I invoke hybridization which means I mix orbitals and I make new orbitals which gives us the suitable geometry required to minimize the lone pair bond pair bond pair 1 pair etcetera repulsions. So please do not say that ah BF 3 is trigonal planar because it uses SP 2 hybridization it is the other way around BF3 uses SP 2 hybrid orbitals of boron because it has to be trigonal planar being an AB 3 molecule and that is determined by VSEPR.

But perhaps I have also put the card before the horse a little bit because out of the blue I started talking about hybridization and hybrid orbitals without telling you what hybridization is, and what am I talking about?



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* $|\alpha|^2 = |\gamma|^2$, $|\beta|^2 = |\delta|^2$
- Hybrid orbitals are ***ortho-normal*** to each other

Hybridization origintes in VBT and relies on experimental results

Well ah this is the more formal ah discussion the handsome gentleman you see here is Linus Pauling's who has been 1 of the founding fathers of the field of chemical bonding especially and ah Pauling's as you might know got 2 Nobel prizes 1 in chemistry 1 in peace very interesting life is a lot of things. ah He wrote this book on chemical bonding which for a long time was a text book and now it has become a classic ah you can read it very easily. I recommend that you read Pauling's book and pauling also proposed this vitamin c theory by which he said that vitamin c is something that protects you from lots of lot of diseases.

He also tried to work in the structure of biomolecules very lustrous carrier extremely significant contribution to science as long as human civilization exists in this present form Pauling's name will not be forgotten. So hybridization was 1 of the concepts that was introduced by Linus Pauling so what he said is that we need more effective bonding. More effective bonding means in this context we need to minimize these bond pair bond pair or whatever repulsions.

To do that since we do not have suitable orbitals we have to produce suitable orbitals by taking linear combinations of atomic orbitals. So, ah this is a schematic energy diagram of 2s and 2p orbitals remember in a multi electron atom I do not remember whether I said it in as many words but what happens in multi electron atoms is that ah because of shielding 2s and 2p electrons now have different energies.

You might remember that S, P these are all atomic orbitals and orbitals as you better remember by now we having said it so many times are 1 electron wave functions. So, as long as its a 1 electron system ah 2 s and 2 p orbitals actually have the same energy but ah in a multi electron atom any electron atom the extent of shielding of 2s and 2p electron is not same that is why 2p electrons have higher energy than 2s electron.

So what Pauling said is that let us mix a required number of orbitals and we can mix them in different ways we can think that we have applied a field which induces mixing. So, let us say we have mixed 1 orbital let us say 2pz orbital generally ah what we do is we take z to be a unique axis let us say we have done mixing of 2s and 2p orbital and we have made 2 orbitals 1 is gamma 2s + beta 2pz the ah sorry alpha 2s plus beta 2pz the other is gamma 2s plus delta 2pz.

So now ah these are hybrid orbitals and the picture that I am showing you here is the general picture and sometimes people actually contest this picture because we are fixated upon thinking of equivalent hybrid orbitals I will come to that. But please believe me for now that this is the most general picture in which you can apply some kind of a field do something or require the molecule to undergo hybridization and ah make hybrid orbitals ah these are coefficients alpha beta gamma delta.

Depending on the relative magnitudes of alpha beta gamma delta the energies of the 2 orbitals are going to be more or less or equal to each other. So ah well more about that shortly. See this coefficients depend on field strength and square of a coefficient is contribution of the atomic orbital and hybrid orbital. So we have discussed linear combination only already we are going to discuss linear combination in the later stage of this course as well.

So what we know is that when we take linear combination and take mod square the contribution comes from mod square of the coefficient. So see ah in this orbital that have drawn as lower in energy mod alpha square or alpha square if alpha is real that is going to give me the s contribution. Mode beta square or beta square if beta is real is going to give me the relative contribution of 2pz. Similarly here gamma square or mod gamma square will give me contribution of 2s mod delta square or delta square will give me contribution of 2pz in this hybrid orbital.

Now suppose mod alpha square is equal to mod gamma square that means the orbitals are equivalent that means they have the same contribution from s orbital same contribution for p orbital as you understand energy of the orbital will depend on since we are mixing now orbitals wave functions that have little different energy from each other ah if the contribution of 2 s is more, then the energy of the hybrid orbital will be closer to that of 2s that is lower in energy.

If contribution of 2s is less then contribution of p is more we say p character is more or p contribution is more than that orbital will be closer in energy to ah few orbitals. So that would be non equivalent but if what we have shown here mod alpha square is equal to mod gamma square mod beta square is equal to mod delta square then you have equivalent hybrid orbitals. So, the hybrid orbitals that we have used many times from class eleven or class twelve sp 2 sp 3 sp these are all equivalent hybrid orbitals.

But it is not necessary that they always have to be equivalent. So in our discussion we will also talk about hybrid orbitals that are non equivalent. We actually encountered them in say water okay orbitals used to ah used in 1 pair you need 2 such orbitals are equivalent of 1 kind orbitals for lone pair are equivalent to another kind. The 2 types are not equivalent to each other. So, this is the most general picture there is no need to think that hybrid orbitals must necessarily always be equivalent.

If they are not equivalent then you cannot use notations like your ah sp sp 2 sp 3 and so on and so forth that is all. Now another important thing to remember is that hybrid orbitals are orthonormal to each other. We make them mix them in such a way and we are actually going to do some calculations so this will become clearer when we do that. We mix them in such a way that they form an orthonormal set.

So take sp orbitals the 2sp orbitals are actually orthogonal to each other and they are normalized by themselves that is how we calculate the coefficients in the first place more about that when we come to it now.

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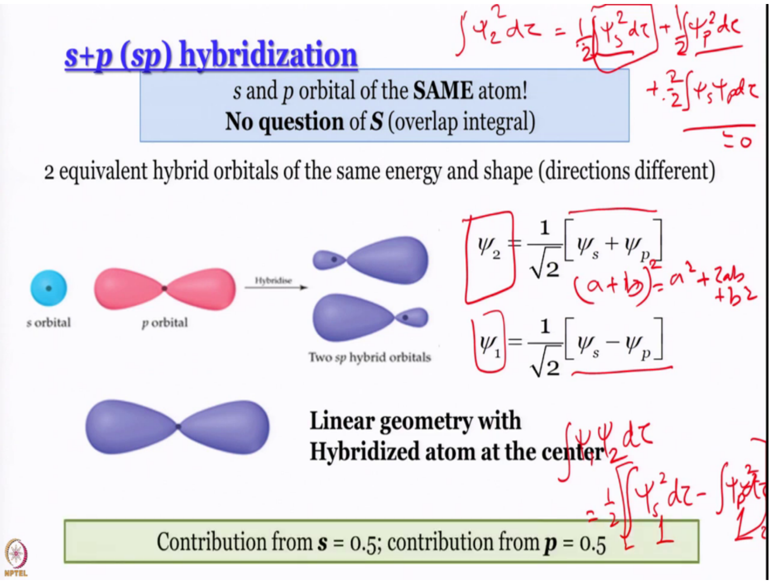

s+p (sp) hybridization

s and *p* orbital of the **SAME** atom!
No question of *S* (overlap integral)

2 equivalent hybrid orbitals of the same energy and shape (directions different)

$$\boxed{\psi_2} = \frac{1}{\sqrt{2}}\left[\psi_s + \psi_p\right]$$

$$\boxed{\psi_1} = \frac{1}{\sqrt{2}}\left[\psi_s - \psi_p\right]$$

Linear geometry with
Hybridized atom at the center

Contribution from ***s*** = 0.5; contribution from ***p*** = 0.5

$$\int \psi_2^2 d\tau = \frac{1}{2}\boxed{\int \psi_s^2 d\tau} + \frac{1}{2}\int \psi_p^2 d\tau + \frac{2}{2}\int \psi_s \psi_p d\tau$$

$$= 0$$

$$(a+b)^2 = a^2 + 2ab + b^2$$

$$\int \psi_1 \psi_2 d\tau = \frac{1}{2}\left[\int \psi_s^2 d\tau - \int \psi_p^2 d\tau\right]$$

$$1 \qquad 1$$

Let us start talking about ah the first kind of hybrid ah well equivalent hybridization that we want to discuss and that is sp orbital hybridization how do I decide whether I want sp or sp or sp3 rule of thumb number of hybrid orbitals is equal to number of participating atomic orbitals. And, ah so if you need 2 equivalent bonds like you do in acidity then I need 1s or s will always be there I need only 1p orbital to mix with s orbital so I used sp.

If you want ah 3 what did I say I say 1 if I have 2 bonds 2 equivalent bonds like in acetylene like in acetylene part was correct then we will do sp hybridization because 1s orbital 1P orbital makes to give you 2 sp hybrid orbitals and how they look we will come to that if I want to talk about BF 3 then I need 3 ah equivalent hybrid orbitals for the 3 sigma bonds. So, then I need 3 orbitals one is s I need 2 of the p's. If I want to talk about methane I need 4 orbitals 4 sigma bonds 1s and all the 3 p's like that.

Now one thing that we should mention here and this becomes most important because we are also going to talk about molecular orbital theory and we have already we already know about overlap integral from our discussion of your ah well take the name overlap integral then ah discussion of many electron atoms ah please do not forget that s and p orbitals are of the same atom. So, overlap integral and all those things does not do not even arise.

Now let us go ahead, so what we need is 2 equivalent hybrid orbitals of same energy and shape directions of of course have to be at 180 degrees to each other because we want to handle AB 2 kind of systems. What do I do this is what I need I have an s orbital and I have a p orbital what I am drawing here is your ah constant probability surfaces not trillion orbitals. So when you hybridize I want to hybridize in such a way that I will get 1 orbital pointing this way the other orbital pointing that way.

So I want a major lobe on 1 side I want a minor lobe on the other side and this black dot is a nucleus please note that the nucleus is within the minor lobe. This another mistake that we sometimes make we place the nucleus at the node it is at the minor load minor lobe and I will convince you that the nucleus is ah in the minor lobe. So, it is very simple I have only 2 orbitals here s and p and when I combine essentially I need linear combination.

So when I have 2 functions I can take 2 kinds of combinations one with minus one with plus and then I want to normalize it. ah I said earlier that the hybrid orbitals have to form an orthonormal set so I take psi s + psi p psi s - psi p 1 by root 2 is normalization constant please check for yourself that psi 2 is normalized psi 1 is normalized not very difficult to see because after all psi s and psi p by themselves are normalized.

So what is your ah integral psi 2 square and should I write x no I will write side to square t tau but I write it in a little short hand notation that will be equal to integral psi s square d tau plus integral psi p square d tau plus integral I am not even writing the constants all or no I think I should so 1 by 2 no this is 1 by 2 and this is going to be psi s psi p d tau this is a 1 by 2 here and 2 I hope you understood what I did this is a + b.

So what is a + b whole square that is a square + 2 ab + b square so this is a square this is 2 ab this is b square but now we are talking about not any a and b we are talking about orbitals. So now see this integral here what is this equal to integral psi square that is equal to 1 because psi s by itself is normalized. So this thing becomes half second one again psi p is normalized this thing becomes half and here psi s and psi p remember are orthogonal to each other so this integral will be equal to 0.

And this is what I said do not get confused with overlap integral will get something like this ah later on when we talk about MO, well even in VBT we have discussed little bit. So, ah we do not think this is overlap integral overlap integral arises only when there are 2 nuclei here there is only 1 nucleus so this is 0 this is 1, this is 1 this is half, this is half, half plus half is equal to 1 so we have proven that psi 2 is normalized.

Similarly you can show that psi 1 is normalized as well and what happens if I try to work out integral psi 1 psi 2 d tau psi s plus psi p this is psi s minus psi p and we have 1 by root 2, 1 by root 2 that will be 1 by 2 integral psi s square d tau minus and take this outside the bracket integral psi p square d tau. So now we know this is 1 this is 1, 1 - 1 is 0, so we have proved that psi 1 and psi 2 actually are orthogonal to each other.

Linear geometry with hybridized atom at the center this is what we achieve when we use sp hybridization but we have unfinished business. I told you that the nucleus actually resides in the minor lobe which means that the way I have drawn it here the minor lobes are actually overlapping with each other. I should actually prove it before we close this discussion. So now see ah contribution from s what is the contribution from s half contribution of p is also half.

So it is an equal mix contribution is 0.5, 0.5 50% s character 50% p character how did I get half 1 by root 2 square remember coefficient square.

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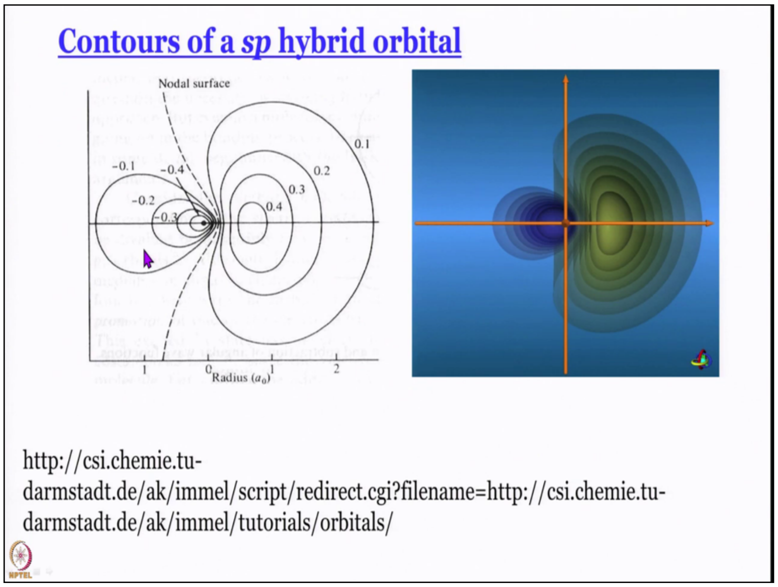

Contours of a *sp* hybrid orbital

http://csi.chemie.tu-darmstadt.de/ak/immel/script/redirect.cgi?filename=http://csi.chemie.tu-darmstadt.de/ak/immel/tutorials/orbitals/

Now let us think about the contours for the moment. This is the contour of sp hybrid orbital and I show you how we get it ah this is where the nucleus is as I said the ah nucleus is actually engulfed by the minor lobe ah um somehow this does not work on my computer but if you go to this link I have not checked it in a while I hope it is still there you can see very nicely how a 2s and a 2p orbital morph into ah giving you this sp hybrid orbital.

And the reason why you get a node here and the reason why you get ah this nucleus engulfed by the minor lobe is that you are working with 2s orbital and 2s orbital itself has a node. So, let us see if you understand that a little better ah from here.

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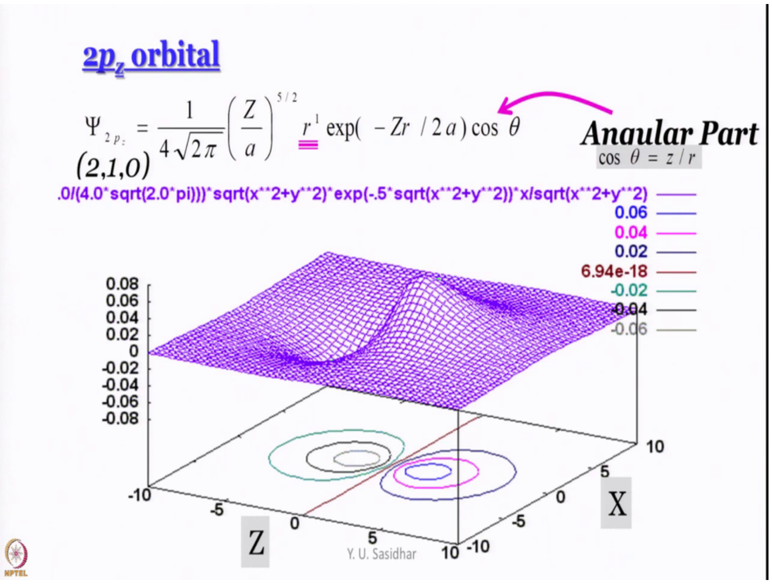

$2p_z$ orbital

$$\Psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{5/2} \underline{\underline{r^1}} \exp(-Zr/2a)\cos\theta$$

(2,1,0)

Angular Part

$\cos\theta = z/r$

Now we go back to very early part not very early part sometime I do not remember module 14, 15, 16 where we had shown you the plots of orbitals against r as I said these are made by professor Shashidaran about 20, 21 years ago so this is the plot of your 2s orbital; 2s orbital has a radial node goes through goes to 0 changes sign and remains negative ah and becomes 0 asymptotically. So this is a radial node and I had shown you the 3d picture ah actually I shown you prettier 3d picture then what you show this black and white picture that I show you here and this is what it looks like.

And you also know that ah this is what the plot of this 2pz orbital would be 3 d plot psi on 1 axis x and z on the other 2 axis we have a hill we have a trough. We have a valley now let us do something let us take a section let us take a razor blade and cut it from the top let us take a section of this to a orbital let us also take a section of this 2 pz orbital you understand what a section is; I am sure you take a ah what should I say ah take a watermelon and cut it.

If you cut it this way you see a cross section that is an oval you cut it this way you see a cross section that is about roughly a circle.

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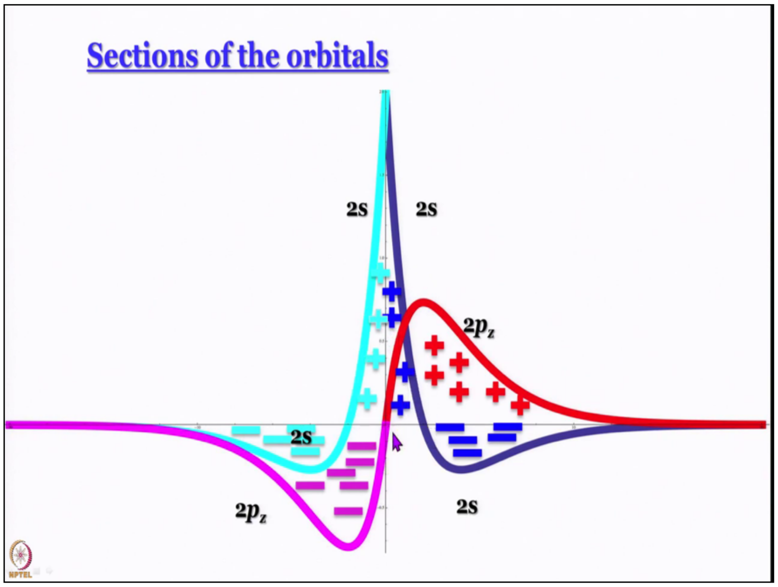

Sections of the orbitals

Similarly we are going to take cross section and this is what we see this here is your 2s peak at the center falls off goes to the node becomes negative then goes from minimum and becomes 0 asymptotically same thing on the other side what about 2 pz plus slope here then at the nucleus we have a node there is a very difficult difference between 2s and 2p, 2s has maximum at the nucleus 2 pz has maximum ah sorry zero node at the nucleus.

And there it changes sign now ah do not forget the question we are trying to answer we are trying to answer the question why are we saying that ah the nucleus is engulfed by the minor lobe. So, now look at the ah periphery of the nucleus and let me acknowledge professor Sandeep Kerr my colleague who actually drew this picture and showed us that this is a good way to explain this. This picture I have not seen it any in any text book.

So now see, near the nucleus what is the value of 2 pz, close to nucleus it is 0 what is the value of 2s near the nucleus it is very high. So, I hope you will agree with me that in the immediate vicinity of the nucleus it is the value of the 2s orbital that is going to predominate as you go further away 2 pz can take over. So, in the immediate vicinity the ah value of 2p 2s orbital is going to predominate. What happens if you go for far away from nucleus on this side or that side.

If you go to that this side you see 2 pz is plus and 2s is negative they cancel each other you have destructive interference. So you eventually reach 0, if you go to this side then both are negative. So, there is constructive interference so your minor lobe is here and I hope I have been able to convince you that all around the nucleus is going to be plus sign which according to this is the sign of 2s orbital near the nucleus and that is the sign of the minor lobe. Usually minor lobe is showing with minus but do not forget that that is just convention we replace psi by minus sign nothing changes psi square mod psi square remains the same.

So ah this is what gives you this kind of major lobe minor loop and nucleus is within the minor loop I hope you have been convinced that this is how it happens.

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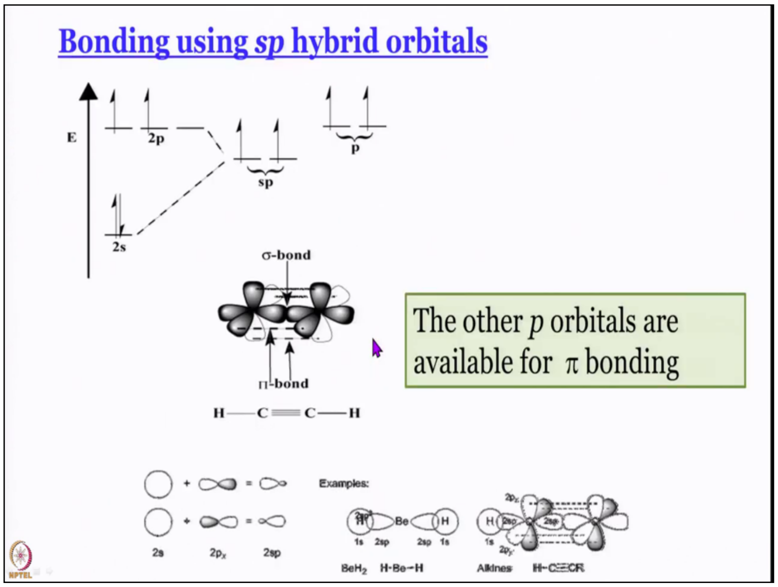

Bonding using *sp* hybrid orbitals

The other *p* orbitals are available for π bonding

All so how does bonding take place you have 2sp orbitals overlapping like this and the remaining p orbitals are available for pi bonding that is why in acetylene you have 1 sigma orbital then 1 pi orbital like this 1 pi orbital like this. Say pz is used for sigma is for hybridization which is used for sigma bonding p x and p y or I should show like this p x and p y are used for pi bonding that is what we have discussed about linear geometry next in the next class we will talk about trigonal geometry and sp2 hybrid orbitals.