Carbon Materials and Manufacturing
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Lecture - 08
Sp$^{(2+n)}$ Hybridization: Curved Carbon

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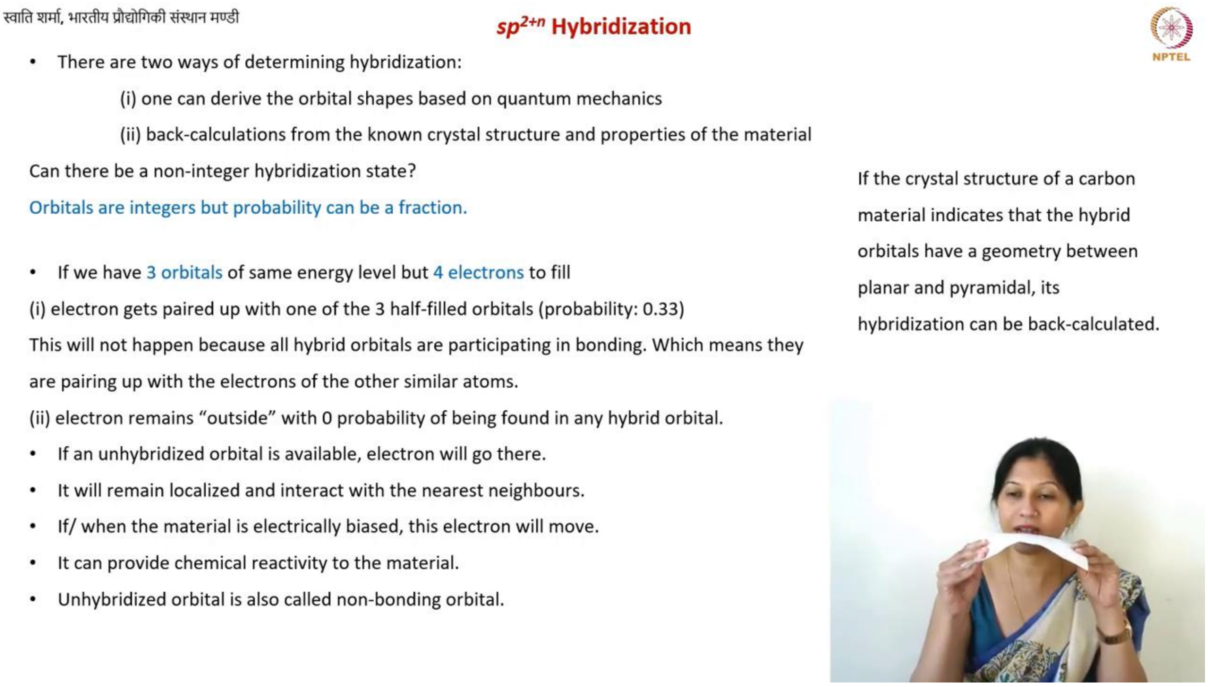

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sp^{2+n} Hybridization

- There are two ways of determining hybridization:
  - (i) one can derive the orbital shapes based on quantum mechanics
  - (ii) back-calculations from the known crystal structure and properties of the material

Can there be a non-integer hybridization state?

Orbitals are integers but probability can be a fraction.

- If we have 3 orbitals of same energy level but 4 electrons to fill

(i) electron gets paired up with one of the 3 half-filled orbitals (probability: 0.33)

This will not happen because all hybrid orbitals are participating in bonding. Which means they are pairing up with the electrons of the other similar atoms.

(ii) electron remains "outside" with 0 probability of being found in any hybrid orbital.

- If an unhybridized orbital is available, electron will go there.
- It will remain localized and interact with the nearest neighbours.
- If/ when the material is electrically biased, this electron will move.
- It can provide chemical reactivity to the material.
- Unhybridized orbital is also called non-bonding orbital.

If the crystal structure of a carbon material indicates that the hybrid orbitals have a geometry between planar and pyramidal, its hybridization can be back-calculated.

Hello everyone. Now let us move on to a very interesting concept that will be useful throughout this course because when you are going to understand the characterization of carbon materials and the manufacturability applications, you will find certain types of carbon structures that are curved. One example of the curved carbon structures is buckminsterfullerene which you already know. Curve means anything that has a curvature. It can be a completely spherical molecule, or it can be something in between. So, it is not completely spherical but let us say you have a certain bending.

So, these kinds of structures are then known as curved carbon structures. Why do they have this kind of curvature? And where does it all starts? We know everything starts from hybridization. If there are hybrid orbitals and they take a tetrahedral kind of kind of geometry, then you have diamonds. If they take a planar kind of geometry then you have your graphite-like structures.

Now, what happens? If they take some geometry in between the geometry of diamond and that of graphite, in that case you have a certain angle which is neither that of the pyramid nor that of the planar structure. You have something in between. And when it happens to several such atoms which have similar hybridization in that case the overall geometry is the curved geometry and that is what we call curved carbon structures. This type of geometry is a result of sp^{2+n} hybridization and that is the topic of today's lecture.

You know hybridization for diamond and graphite and we also previously talked about the orbitals. How do we determine hybridization? Well, there are two methods. So, one method is that we actually mathematically derive the shapes of the orbital by solving Schrödinger's equation for the hydrogen atom, this is the standard thing. So, this is basically the quantum mechanical approach that is how you know the shape of the orbital. There are also methods of experimentally validating based on the chemical reactivity of a certain type of material. You can also validate these shapes of the orbitals, but they are quantum mechanically derived.

Now, in the case of manufacturing materials, we can back-calculate the hybridization states based on the geometries of crystals. This is something clear to us that the crystal geometries are basically nothing but sort of large-scale geometries that we have also at this hybridized molecular orbital level.

So, we know this shape for graphite and for diamond and if there is something in between can we really back-calculate the hybridization state. And if we do then what are the values that we get and this is what we are going to learn in this particular lecture.

So, we are going to use method number 2. Can we also do this quantum mechanically using method number 1? Yes, but there we have to understand that again the number of orbitals is an integer number, but the probability of finding the electron in those orbitals can be a non-integer value. So, this is exactly what I have written here. We talked about these unhybridized p orbitals, In the case of graphite, we have 3 orbitals that get hybridized and they participate in bonding. In the case of diamond, all 4 orbitals get hybridized and they form 4 molecular orbitals which are then filled basically.

All of these electrons participate in bonding and they do not remain free afterward, they are not really interested in doing anything else because they have already paired up and formed a bond. So, these are σ bonds that is how we have the sp^3 type geometry or sp^3 type crystals.

But in the case of graphite, it becomes interesting. Now, you have this unhybridized p orbital. What is interesting for us is to figure out what is the probability of finding the electron in that unhybridized p orbital. As such if there is no other option for the electron then that probability is going to be 1. But what if there is some option? if the electron can potentially also go somewhere else, in that case, the probability will be less than 1. That probability will not be an integer number and that is how you can get these fractional probabilities and therefore, fractional hybridization states.

So, that would be the quantum mechanical approach based on this idea you can also calculate the hybridization states. But when we talk about materials in manufacturing aspects, it is easier for us to back-calculate the hybridization from the crystal geometries.

Because the crystal geometries are important for us and when we are performing manufacturing on any given material, these crystal geometries can also be observed at a larger scale. For example, if you are polishing or cutting a diamond the cutting patterns and the slip planes of diamonds will be according to the crystal structure.

Similarly, when you know a graphite crystal, you know that these basal planes of graphite that we will in detail learn about the crystal structure of graphite, the planes of graphite can slide on top of each other, you have this layered structure.

You know the single layers are very strong but when they are stacked on top of each other then bonding between them is not very strong. So, this already gives you an idea of the bonding. So, even if you did not know the material or if you did not know what type of hybridization it possesses, even in that case just by observing the behavior of the material at the time of manufacturing you can understand the type of hybridization it can have. So, it is as I said easier for us to back-calculate the hybridization.

We are also going to often encounter carbon materials that are curved, but buckminsterfullerene being the most common example. So, we can also now back-calculate the hybridization from there. Let us try to do it in this particular lecture.

So I will start within with some examples. Let us say we have 3 hybrid orbitals and we have 4 electrons, right. These 3 orbitals are hybridized orbitals, so they all have the same level of energy. Basically these 4 electrons can choose to go into any of these 3 orbitals. What will happen in this scenario? You have 4 electrons and 3 orbitals, 3 of these electrons will go into 3 orbitals first and now these 3 orbitals are half-filled. What happens to the 4th electron? This 4th electron can go into one of these 3 orbitals which were half-filled till now and then gets paired up. What would be the probability of this event? 0.33 or 1 by 3.

But this will actually not happen, because when we think of it theoretically it can happen. But it will not happen in practice because of the fact that hybridization only takes place at the time of bonding which means that there is another carbon atom nearby, that carbon atom will also have three sp^2 type orbitals, let us say this is an example of sp^2 type orbital when I say 3 hybrid orbitals of the same energy level.

So, let us say these now these two atoms will come close together and they will form 3 σ bonds and that is how you will have the pairing up of the molecular of the electrons in the molecular orbital. This means that the 4th electron that cannot go into any of these 3 orbitals anymore. They are completely filled with electrons. They have paired-up electrons.

So this particular scenario will not really take place if we are talking about hybridization or hybrid orbitals. This could take place if there was if this was not happening at the time of bonding. So, if we were not talking about hybridized orbitals, in that case the 4th electron could have the 0.33 probability of going and pairing up. But that is not the scenario we are talking about 3 hybrid orbitals, ok. So, this will not happen.

Now, the other possibility for the electron, the one and only possibility is that it remains outside of these 3 bonding orbitals or bonding electrons. So this electron remains in the unhybridized p orbital if we have one. So, if this is an example of sp^2 type of orbitals then we do have one unhybridized p orbital. Now your remaining electron will have a 100 percent probability of being found in that unhybridized orbital. This is the scenario when it comes to graphite, we are talking about perfect graphite. However if this electron can also potentially occasionally go to another neighboring orbital or let us say unhybridized p orbital of another neighboring carbon atom or if it can occasionally also go into the hybridized orbital or it can basically occasionally change its position with another electron. If there is a probability for this particular electron to go into another orbital hybridized or unhybridized. In that case the overall probability of that electron being found in the unhybridized orbital is not 1, it is less than 1.

So, this kind of event can take place in some carbon materials when there are neighboring unhybridized orbitals available. So, this is in fact what happens in most of the cases and that is why we have this π band and the electron is not always localized to its parent atom. It is not always localized, it does interact with its nearest neighbors and that is why it may have less than 100 percent probability of being found in the unhybridized p orbital of its parent atom.

Now, whenever we apply any kind of electrical bias or we apply any other kind of force then this electron, which is definitely not participating in bonding, this electron can potentially move. That is why we call it a free electron. Yes this electron is available for electrical conductivity as long as it has a high enough probability of remaining free. It also can provide chemical reactivity and many other properties to the material and is of course this is a non-bonding electron.

However, now if you have a certain type of crystal structure in your carbon material, which has its geometry between the pyramidal geometry of diamond and the planar trigonal planar geometry of graphite. In that case, the probability of finding the electron in the unhybridized p orbital is less than one. It basically indicates that the probability is less than 1. Because if you had the geometry like diamonds, in that case we had 4 hybrid orbitals. But in the case of geometry when you have 3 hybrid orbitals which is like graphite, you have one completely unhybridized orbital.

Now, if you have something in between, that means unhybridized orbital is also somewhere in between completely hybridized and completely unhybridized orbital. This means the probability of finding the electron there is also somewhere in between. It is a non-integer number and that is when we can back-calculate the hybridization states.

So, in which type of structures will this happen? Now as I mentioned you do not have the pyramid let us say if I take the bottom part of the pyramid is how it looks. And the angle between these two sides is 109.5, in the case of graphite it looks like this, so this angle is 180. If you have something in between that is what we are now we are discussing and that is when you have the non-integer hybridization state and sp^{2+n} hybridization state. So, I hope it will become more clear from the next couple of slides.

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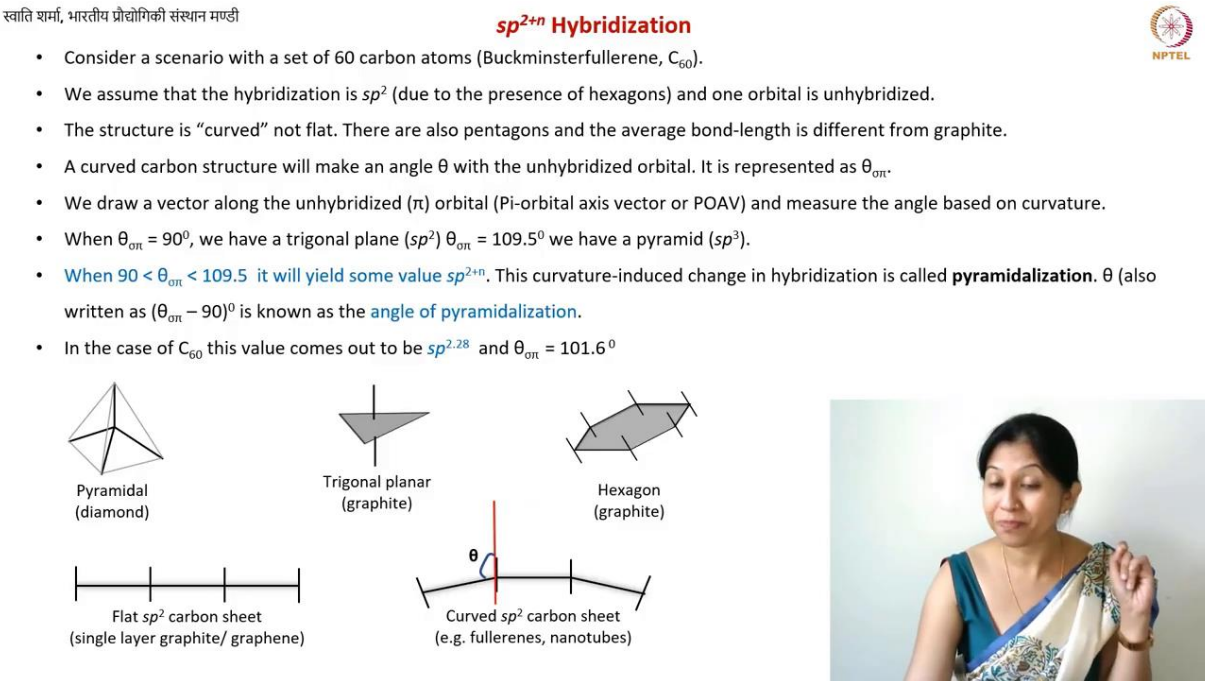

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sp^{2+n} Hybridization

- Consider a scenario with a set of 60 carbon atoms (Buckminsterfullerene, C_{60}).
- We assume that the hybridization is sp^2 (due to the presence of hexagons) and one orbital is unhybridized.
- The structure is "curved" not flat. There are also pentagons and the average bond-length is different from graphite.
- A curved carbon structure will make an angle θ with the unhybridized orbital. It is represented as $\theta_{\sigma\pi}$.
- We draw a vector along the unhybridized (π) orbital (Pi-orbital axis vector or POAV) and measure the angle based on curvature.
- When $\theta_{\sigma\pi} = 90^0$, we have a trigonal plane (sp^2) $\theta_{\sigma\pi} = 109.5^0$ we have a pyramid (sp^3).
- When $90 < \theta_{\sigma\pi} < 109.5$ it will yield some value sp^{2+n}. This curvature-induced change in hybridization is called **pyramidalization.** θ (also written as $(\theta_{\sigma\pi} - 90)^0$ is known as the angle of pyramidalization.
- In the case of C_{60} this value comes out to be $sp^{2.28}$ and $\theta_{\sigma\pi} = 101.6^0$

Now let us take the example of buckminsterfullerene. So, this is a very well-known curved carbon structure. And it contains 60 carbon atoms. So, this is one big molecule that contains 60 carbon atoms. This is something very special about carbon that we have a large sheet and chain-like molecules. And that why I am saying this because these 60 carbon atoms are not completely independent of each other. Because this is one large molecule that these 60 carbon atoms are bonded to each other.

And what is also interesting is that the unhybridized p orbital although it is localized and belongs to each carbon atom. There is a probability that the electrons from the unhybridized orbital of one atom interact with that of the neighboring atom, and the neighboring one will interact with its next neighbor and so on. And we also do not completely know for how long is the influence of this interaction.

So, the nearest neighbor interaction is not only with the cases of curved carbon structure, but also in the case of graphite and graphene. We do not know if the electron only participates with its next carbon atom or let us say the next two carbon atoms or the next 5 carbon atoms.

This is something we have tried to understand it very recently in the case of graphene i.e single layer of graphite. What I am trying to say here is that your 60 carbon atoms are not independent and the electron in the unhybridized orbital is definitely interacting with the other nearby orbitals as well.

If we want to back-calculate the hybridization, we need to understand what kind of structures we have. We first need to assume something about our molecule. So we assume that it has the sp^2 type hybridization rather than sp^3, because well there is a free electron available. And also because there is a significant number of hexagons present, that means there are some sp^2 hybridized carbon atoms.

In fact, that is the reason you will often hear people say that if you take a graphene sheet and you roll it up, it becomes a carbon nanotube or if you make a football out of it becomes a fullerene. This is just for an easy representation. This is not completely true. You cannot actually make a football from a sheet that contains only hexagons.

In fact as an exercise, you can even try to do that. You can actually look at a football and you will see that it has also you know a large number of pentagons. If you had only hexagons then you will have a flat sheet, you cannot really make a completely spherical structure. You can provide a little bit of curvature perhaps, but you cannot make a sphere out of a structure that has only hexagons.

Anyway, we are going to assume that we do have one unhybridized p orbital and that is why we start with this sp^2 assumption of hybridization. But now we know that the structure does contain some pentagons or some non-hexagonal structures otherwise we will not have any curvature.

Here I have described it with some images. So, this is your pyramid. This is the sp3 hybridized structure, this is your diamond when you have no unpaired or unhybridized orbital available. But in the case of graphite, you have one unhybridized p orbital on top and bottom, that is what I have shown with the lines. And then you have 3 electrons that have participated in bonding so that they are in your trigonal planar positions.

Now, with these triangles we learned in the graphite lecture that we can make hexagons. If two triangles come close to each other then we often have these hexagon kinds of structures and that is why we have all of these hexagons in your graphite-like structure. So, here I have drawn one hexagon, and all of these lines indicate the unhybridized p orbital of all 6 carbon atoms which are present in that hexagon.

Now, we will talk about curved carbon structures. So, curved carbon structures will make some angles In the case of graphite you will have a flat hexagon. But in the case of curved carbon structure, it will not be flat there will be some angle. And here in this illustration, I will show you where this angle belongs(refer to video). You see that you have some sort of curvature.

One more important thing before we go into this angle and is that when we talk about the curvature, we are assuming that this structure is a polyhedron structure and not a complete sphere. So, you will see the lines that I have drawn here it is like this and then this(refer to video). It is not like a smooth transition. It is not a complete you know smooth sphere.

So, let me give you an example of a 2D geometry of a similar type. If you have 3 lines you make a triangle. If you have 6 lines you make a hexagon. If you have infinite lines in that case you will get a circle. But if you do not have infinite lines, let us say you have 60 lines, in that case you will get the structure of a polyhedron that has 60 lines. But you can still have well-defined separate 60 lines.

So, if now think of the same thing in 3D, instead of a circle now think of a sphere. So, if we have an infinite number of these hexagons and pentagons kinds of structures hexagons then you would have a perfect sphere, but that is not the case. What we have is 60 small geometries, so what we have is a polyhedron kind of structure. This is important for you to understand. Otherwise, it will be very difficult to measure that angle.

So, how do we calculate the angle? You see this red line here. The angle is calculated with respect to the unhybridized p orbital. So, that is why I have drawn this line here. And now you will have the angle between the pentagon or hexagon whatever you have here and the unhybridized p orbital. So, with respect to that if you calculate the angle θ that is what is the angle which must be between 109.5° and 90° which is the case for diamond and graphite. But this angle is now between the geometries of graphite and diamond.

So, this red line that I have drawn along the unhybridized p orbital we call it π-orbital. So, this particular vector is known as the π-orbital axis vector or POAV. And the π-orbital axis vector helps us to calculate the curvature of any given carbon molecule.

Now, when this value θ by the way is also called θσπ because this is the angle between the σ type bonds and the π type bond. So, this θσπ will be 90 in the case of graphite and it is going to be 109.5 in the case of pyramid shape structure or in the case of sp^3 hybridization.

And of course, in the case of anything which has sp^{2+n} type hybridization, that is between sp^2 and sp^3 then your angle is going to be between the angle of sp^2 and sp^3. This angle is known as the angle of pyramidalization.

What is pyramidalization? Because you had a plane so why do we call it pyramidalization? Because you had a flat structure and now you are going towards the pyramid. So, at some point, you have the pyramid. So that is why it is called the angle of pyramidalization.

And this angle by the way often is calculated as θσπ-90, but you know this is the angle that we calculate. Why do we say minus 90? There is no specific reason. Just gives you slightly smaller values that are easier to understand. When you call θσπ - 90 as the angle of pyramidalization that case it will be 0 for graphite and 19.5 for diamond.

But, in this lecture, I am going to use the overall value of θσπ rather than calling rather than using θσπ - 90. So, in the case of C60 the value of θσπ is 101.6° and θσπ - 90 will be 11.6°. And if you back-calculate from here then you are going to get the value $sp^{2.28}$ for the hybridization.

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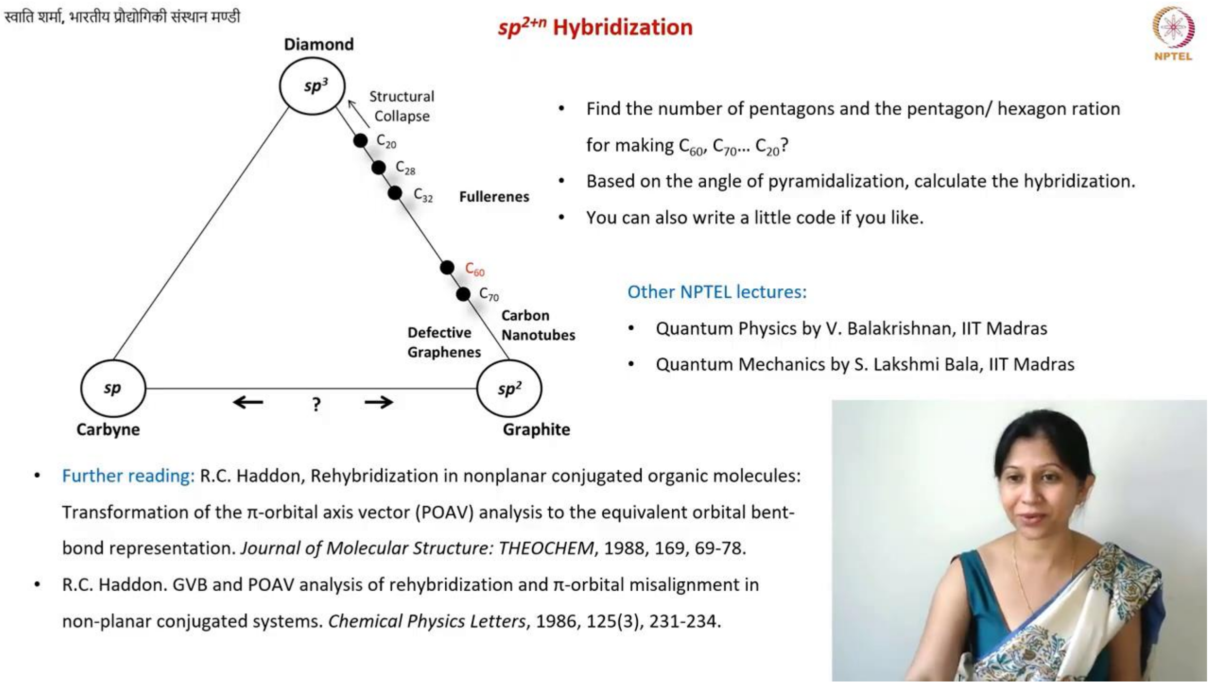

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sp^{2+n} Hybridization

- Find the number of pentagons and the pentagon/ hexagon ration for making C_{60}, C_{70}... C_{20}?
- Based on the angle of pyramidalization, calculate the hybridization.
- You can also write a little code if you like.

Other NPTEL lectures:

- Quantum Physics by V. Balakrishnan, IIT Madras
- Quantum Mechanics by S. Lakshmi Bala, IIT Madras

- Further reading: R.C. Haddon, Rehybridization in nonplanar conjugated organic molecules: Transformation of the π-orbital axis vector (POAV) analysis to the equivalent orbital bent-bond representation. *Journal of Molecular Structure: THEOCHEM*, 1988, 169, 69-78.
- R.C. Haddon. GVB and POAV analysis of rehybridization and π-orbital misalignment in non-planar conjugated systems. *Chemical Physics Letters*, 1986, 125(3), 231-234.

Now, in this particular diagram, I have made a triangle where I have sp type structures, sp^2 type structures in sp^3 type. You know what are the primary representative examples of each one of them, well carbyne for sp type, graphite for sp^2 and diamond for sp^3. And we know the geometries of each one of them.

Now, if you see between diamond and graphite that is where you have all of these fullerenes like structures. So, these are all the structures with sp2+n type hybridization. What is very interesting is that also their properties are between you know the properties of sp2 and sp3 type carbon materials, for example, diamond is insulator and graphite is a is an electrical conductor, but fullerenes are most of them are semiconductors.

So, their properties are also kind of in between the two types of geometries because after all properties are defined by the crystal structure at a larger scale and the availability of electrons. For example, for conducting electricity, thermal properties, magnetic properties and many other properties, the free electron plays an important role.

Now, what will happen if you keep on increasing the curvature or if you keep on increasing the angle of pyramidalization. Let us say in the case of C60 you have 11.6, anything below 11.6 is also possible. If you have a little bit of curvature after graphite, you can have a sheet that is more like a tube. It does not have much curvature so that it converts into a sphere, but it can have a little bit of curvature. So it will be some sort of curved carbon structure. Maybe it is just a kind of a wavy sheet. You can have this kind of random shape, you can have little bit less or little bit more curvature.

However, when the curvature increases a lot then at some point your fullerene-like structures collapse into sp^3 type structures. So, this again does not physically or experimentally happen. You will not see that if you keep on decreasing the size of the fullerene and then you get diamonds. It does not happen experimentally, but theoretically the structure cannot withstand more than a certain curvature then having diamond-like geometry will be more stable for it. So, we call it is a structural collapse that is why it is people have observed very small fullerene-like structures down to C20, but if you go even further smaller and smaller then rather diamond-like geometry will be preferred which will be thermodynamically more stable for that given carbon molecule.

So, from this diagram now you can also figure out if there is there should be any possibility of carbon structures between sp and sp^2. If there is something between sp2 and sp3 then there should be also something between sp and sp^2 or there is at least a possibility. And in fact many such carbon allotropes or structures have been proposed and there are some of hypothetical compounds and some of them are have been experimentally observed as well.

So this kind of chart tells you that there is a possibility of finding so many different types of structures in carbons. And now all of these structures basically are found in bulk carbons and that is why sometimes when you have bulk carbons which are physically amorphous, it is really difficult to point out what kind of hybridization states do they have because they may actually contain smaller structural units of different types of hybridization. If you see the bond lengths in those carbon materials, they will have a Gaussian distribution. There will be all kinds of bond lengths.

If you keep on heating that material somehow you can induce more sp^2 hybridization. In that case, you will see that the fraction of sp^2 type bond length is increasing, but you will still always have some bond lengths which are not exactly that of the diamond or that of the graphite.

So the point is that all of these sp^{2+n} type carbon structures, we call them curved carbon structures. At least in this course I am going to use this terminology curved carbon because these carbon structures often have physically certain curvature. And they will make some very interesting carbon materials, for example non-graphitizing carbon materials. This is going to form a large section of this course.

Now, I will give you a few little mathematical exercises for you to do, first of all, find out the number of pentagons in different types of fullerenes, at least the completely closed fullerenes. So, if you take C60, C70 or you go down to C20, try to find out how many pentagons will it require to form that kind of sphere, this is exercise number 1.

What you can also do is you take different angles of pyramidalization and try to back-calculate the hybridization states. What you can also do is well if you already have all these calculations you can write a little code where you can you know just enter the value of hybridization and then back-calculate the geometry or the other way around.

So, now I will tell you a few options for further reading. The credit goes for this angle of pyramidalization to R. C. Haddon. He has multiple publications on this topic. I have mentioned two publications, but you can also you can simply search for π-orbital axis vector and Haddon and you will actually find a number of publications from there. Also, in these publications the chemical reactivity of fullerene has been associated. And based on the hybridization states now the chemical reactivity can also be back-calculated, ok.

Also, there are some other NPTEL lectures. I had also mentioned in one of the previous lectures that will tell you a few things about where can you learn more about quantum mechanics and orbitals. So, there are a couple of lectures that I have mentioned. Of course, there may be some other lectures as well where you can learn more about quantum mechanics and the shapes of orbitals and how do we derive the orbital shapes.

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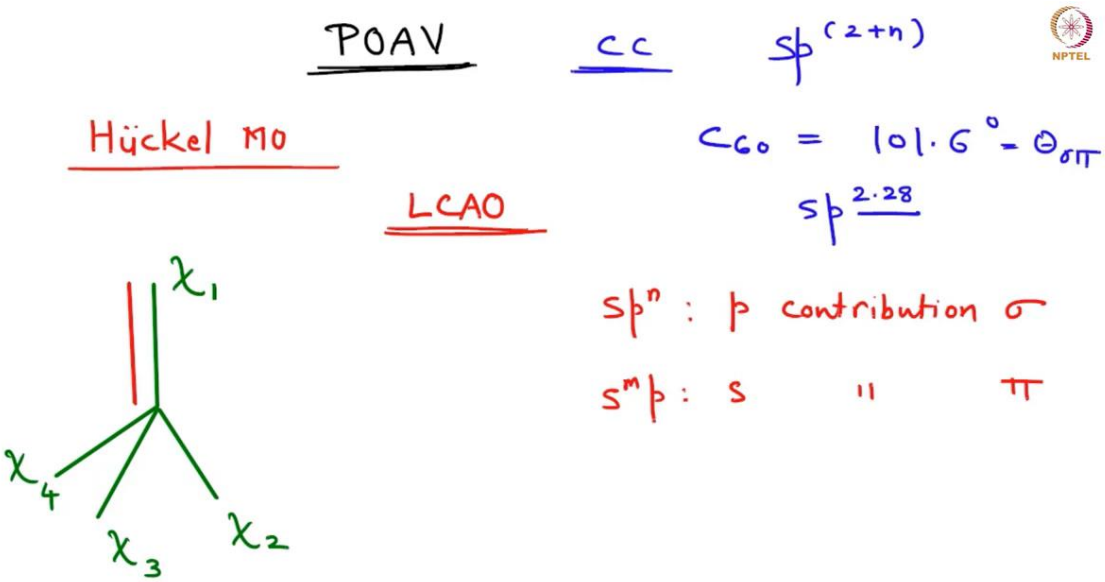

I told you that in the case of manufacturing materials we often back-calculate the hybridization using the geometry of a certain crystal or a certain structure. But it is not as straightforward. It is not just a mathematical numerical or average of sp^2 and sp^3 type of hybridizations. So, I will give you an example. In the case of C60 the angle as we have also discussed in the class that 101.6° is the $\theta\sigma\pi$. However, the hybridization is $sp^{2.28}$. So, from there itself you can probably guess that the hybridization is not just a direct average based on the angle. Then how do we calculate these things? This is done using some computational methods and typically in quantum chemistry courses, you can find more details about these methods. But one very common method is known as the Huckel molecular orbital theory.

Now, I will not be going into the details of the Huckel theory because it is beyond the scope of this course and I am personally not an expert in this area. However, you can find various NPTEL lectures or any other resources for understanding the Huckel theory.

What I am going to do here is, I am going to explain it just in the context of curved carbon structures. I am going to just write down the general expressions for sp^2, sp^3, and sp^{2+n} type of hybrid orbitals. What do I mean by that? Typically hybrid orbitals are written as linear combinations of atomic orbitals. So, hybrid orbitals are your molecular orbitals. This is what we do in the Huckel molecular orbital theory, we write these orbitals as a linear combination of the atomic orbitals that are participating in the formation of that molecular orbital. Now, when we write that specifically in the case of carbon we write down the contributions of s-type orbitals and also the p-type orbitals.

Typically, for finding out you know any details of the hybridization you try to find what is the p contribution. So, what is the p contribution when it comes to your σ bonds? And what is the s contribution in your π bonds? That is why you will write sp^n for finding the p contribution in σ and s^mp when we are talking about the s contribution in π bonds.

Now, what I am going to do is I will draw again our hybrid orbitals. So, we make again this pyramid-like structure. This is a general case and by general case I mean that we can use it for sp^3 and sp^2 both. But in the case of sp^2, this orbital hybrid orbital let me call it χ_1(refer to slides).

So, in the case of sp^2 this χ_1 will be your unhybridized p orbital, in the case of sp^3 this is one of the hybrid orbitals, ok. So, χ_1, χ_2, χ_3 and χ_4 are my 4 hybrid orbitals in a general case. And the χ_1 as you can already see is parallel to your π-orbital axis vector. So, basically this is parallel to the pz.

Now I will write down the expressions for linear combinations of these atomic orbitals for all 3 cases sp^2, sp^3, and sp^{2+n}.

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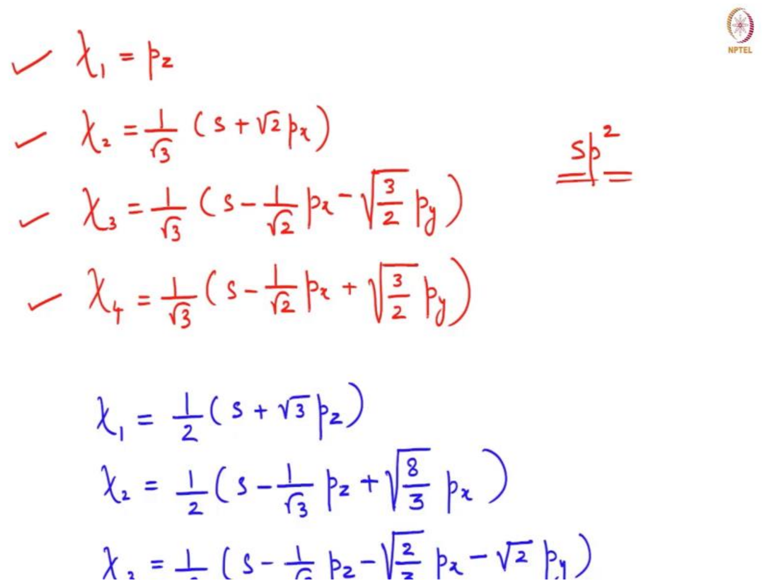

✓ $\chi_1 = p_z$

✓ $\chi_2 = \frac{1}{\sqrt{3}}\left(s + \sqrt{2}\, p_x\right)$

✓ $\chi_3 = \frac{1}{\sqrt{3}}\left(s - \frac{1}{\sqrt{2}} p_x - \sqrt{\frac{3}{2}}\, p_y\right)$

✓ $\chi_4 = \frac{1}{\sqrt{3}}\left(s - \frac{1}{\sqrt{2}} p_x + \sqrt{\frac{3}{2}}\, p_y\right)$

$\underline{\underline{sp^2}} =$

$\chi_1 = \frac{1}{2}\left(s + \sqrt{3}\, p_z\right)$

$\chi_2 = \frac{1}{2}\left(s - \frac{1}{\sqrt{3}} p_z + \sqrt{\frac{8}{3}}\, p_x\right)$

$\chi_3 = \frac{1}{\ }\left(s - \frac{1}{\ } p_z - \sqrt{\frac{2}{\ }}\, p_x - \sqrt{2}\, p_y\right)$

So, the first expression is for the sp^2 type hybridization. Here you can already see that your χ_1 is nothing but your p_z orbital itself or the π-orbital x axis vector. But the expressions for χ_2, χ_3, and χ_4 are the ones that are calculated using the computational methods.

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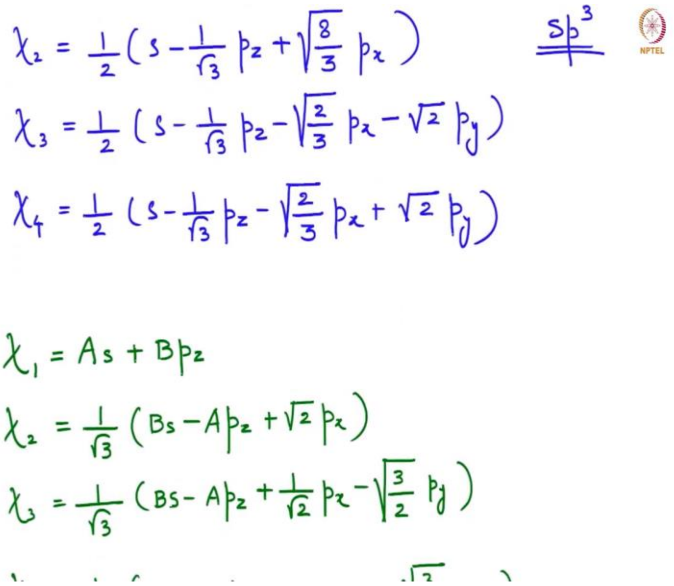

$$\chi_2 = \frac{1}{2}\left(s - \frac{1}{\sqrt{3}}p_z + \sqrt{\frac{8}{3}}\,p_x\right)$$

$\underline{sp^3}$

$$\chi_3 = \frac{1}{2}\left(s - \frac{1}{\sqrt{3}}p_z - \sqrt{\frac{2}{3}}\,p_x - \sqrt{2}\,p_y\right)$$

$$\chi_4 = \frac{1}{2}\left(s - \frac{1}{\sqrt{3}}p_z - \sqrt{\frac{2}{3}}\,p_x + \sqrt{2}\,p_y\right)$$

$$\chi_1 = As + Bp_z$$

$$\chi_2 = \frac{1}{\sqrt{3}}\left(Bs - Ap_z + \sqrt{2}\,p_x\right)$$

$$\chi_3 = \frac{1}{\sqrt{3}}\left(Bs - Ap_z + \frac{1}{\sqrt{2}}p_x - \sqrt{\frac{3}{2}}\,p_y\right)$$

Now, the expressions for sp^3 type orbitals. Now, here in this case because all 4 orbitals are hybridized, then you also have a different expression for χ_1. So, this is the case for sp^3 type orbitals.

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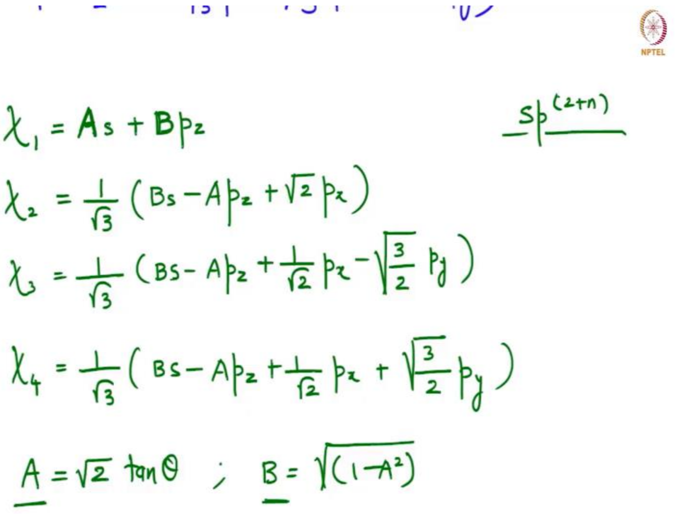

$\underline{sp^{(2+n)}}$

$$\chi_1 = As + Bp_z$$

$$\chi_2 = \frac{1}{\sqrt{3}}\left(Bs - Ap_z + \sqrt{2}\,p_x\right)$$

$$\chi_3 = \frac{1}{\sqrt{3}}\left(Bs - Ap_z + \frac{1}{\sqrt{2}}p_x - \sqrt{\frac{3}{2}}\,p_y\right)$$

$$\chi_4 = \frac{1}{\sqrt{3}}\left(Bs - Ap_z + \frac{1}{\sqrt{2}}p_x + \sqrt{\frac{3}{2}}\,p_y\right)$$

$$\underline{A} = \sqrt{2}\tan\theta \quad ; \quad \underline{B} = \sqrt{(1 - A^2)}$$

And finally, the important one is the general case for the sp^{2+n} type orbitals or hybridization. So this is the general case.

Now here importantly you will see that we have two constants A and B. Because we do not know what the contribution is, again these can be any value of n because this is a general case. So, here we need to just assume two constants say A and B here, and then we write down the contributions of the orbitals in terms of A and B and ultimately calculate the values of A and B.

So, this was just to give you an idea of how we find out the values of n in the case of sp^{2+n}. If you are further interested, I would recommend that you go through some of the computational chemistry courses.