Carbon Materials and Manufacturing
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Lecture - 06
Hybridization in Carbon Atoms

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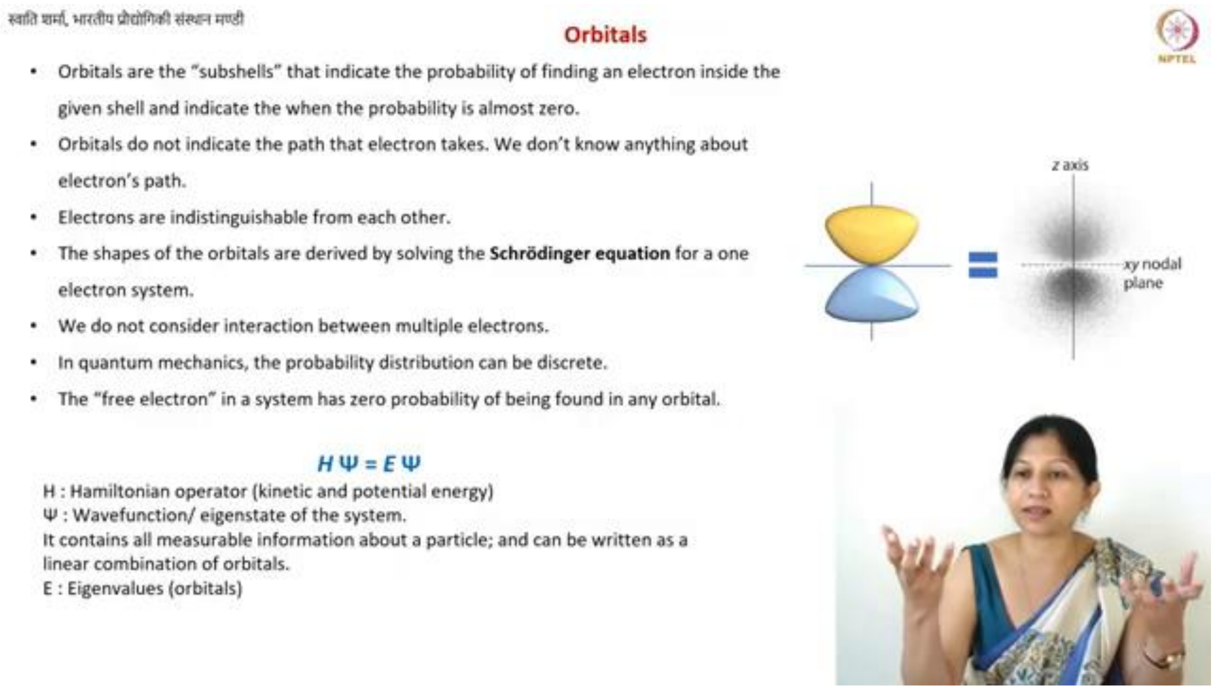

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Orbitals

- Orbitals are the "subshells" that indicate the probability of finding an electron inside the given shell and indicate the when the probability is almost zero.
- Orbitals do not indicate the path that electron takes. We don't know anything about electron's path.
- Electrons are indistinguishable from each other.
- The shapes of the orbitals are derived by solving the **Schrödinger equation** for a one electron system.
- We do not consider interaction between multiple electrons.
- In quantum mechanics, the probability distribution can be discrete.
- The "free electron" in a system has zero probability of being found in any orbital.

$$H\Psi = E\Psi$$

H : Hamiltonian operator (kinetic and potential energy)
Ψ : Wavefunction/ eigenstate of the system.
It contains all measurable information about a particle; and can be written as a linear combination of orbitals.
E : Eigenvalues (orbitals)

Hello everyone. In this lecture, we are going to discuss the concept of Hybridization. So, hybridization is important for various elements, but in the case of carbon, this is basically responsible for all the properties of carbon materials right. And also when we talk about properties, then the application areas are very strongly connected to the properties. And we also have the manufacturability that is connected to the properties because manufacturability is strongly influenced by the crystal structure of carbon. And why do we have different crystal structures of the same element? Well, that is all because of the hybridization at the atomic level.

So, what is hybridization? When two atoms come together, they have some sort of merging of their energy levels, that is what we call hybridization and these energy levels are called hybrid energy levels where the electrons are redistributed. We will get into that before we talk about, what are orbitals.

So, in the previous lecture I told you few things about the electronic configuration of carbon. We also discussed different isotopes of carbon you now know that ^{13}C and ^{14}C also have their own application areas. Now, what we are talking about is the bulk carbon material. Bulk carbon is the materials that are available to us for manufacturing purposes.

So, they mainly contain carbon-12, they may have some ^{13}C and ^{14}C as well, but we do not worry about that for now; what we need to understand is now how carbon behaves at an electronic level. So, we do not think about the nucleus anymore. You must have learned about orbitals. You also probably know few fundamental things about the idea of hybridization as well.

What you learned is there is some sort of nucleus, which is correct. So, you have a nucleus that contains protons and neutrons, and other nucleons. And then around that nucleus, you have electrons that are circling or that are orbiting in a certain, let us say circular path. This is the Niels Bohr model that most of us learn at the school level.

The model has a lot of advantages. It is also a very convenient model for explaining the atomic structure and it does justify a lot of chemical properties of the materials. However, the idea that electrons are taking a certain path or they are orbiting around the nucleus is incorrect.

Why is it incorrect? Because orbitals are not any given path. They are basically nothing but probability density functions. What does that mean? That means, there is a certain region in space where you have the highest probability of finding an electron.

We do not know anything about the path that the electron takes. So, let us take the example of an s orbital. You know that orbitals are subshells. I have also written here what are four quantum numbers. We know that the principal quantum number will define a shell and within this shell, then you have certain subshells.

So, these are discrete energy levels where you can find the electron. These discrete energy levels are what we call the electrons and that is what I am saying is the region in space where you have the probability of finding the electron.

Now let us take the example of s orbital. We have a spherical shape for this function. What does this mean? At any given point if I try to find my electron, then I will find it within that sphere. So, I will find it here, after some time here and then here and then here, and so on. If I do this an infinite number of times and every time I find the electron, I mark a point there. In that case, all those points will be confined within that sphere. Now, might have a higher probability density closer to the core of that sphere and as we go far from the nucleus then we also have a lower probability or smaller probability.

However, the area or the confined region where we will find the electron. that is what we call the orbital. Now, as I said that we do not know anything about the path of the electron. So, when I was saying that we find the electron here and then after some time here, I do not know how my electron went from one place to another place? I do not know if it took a circular path? I do not know where did it go? I really do not know anything about the path of the electron. So, this is something that you need to keep in mind.

Electrons are indistinguishable from each other. Indistinguishable means? If I have let us say 5 electrons in a certain system, I never can say accurately that this is that electron and this is that electron. The electrons might be exchanging places we do not know. We cannot tell one electron from another.

So, we cannot differentiate between two electrons. This does not mean that we do not have 5 electrons. We do have 5 electrons and they are 5 different electrons, but we can never say for sure that the electron that I find in this place was that electron. So, they are indistinguishable from each other.

Now, how do we find out these shapes of the electron orbitals? So, I told you that s orbital is spherical, you also know that when we talk about p orbital, we have this dumbbell kind of shape. And also in that dumbbell, there is a node, a node is a place where you have the zero probability of finding an electron.

How did I come to know these shapes? There are certain experimental methods, there are also certain simulations that you can perform, and you can kind of guess the probabilities of finding the electron in a certain region. But fundamentally the shapes of the electrons are derived from an equation known as the Schrödinger equation.

The idea of Schrödinger equation is not something that I am going to cover in this course, I will be providing you with some NPTEL lectures where you can learn it and of course, there are many other resources also from where you can understand the quantum mechanical aspects and how do we solve the Schrödinger equation.

Here I have mentioned a very general form of this equation. You can also have time-dependent equations. This is just the very general time-independent Schrödinger equation that I have written here:

$$H\Psi = E\Psi$$

H: Hamiltonian Operator

Ψ: Wavefunction/Eigenstate of system

E: Eigenvalues

So, now, I am going to describe the meaning of different terms here. H is the Hamiltonian operator.

So, what is an operator and what does it indicate? So, let us say in classical mechanics if you have a particle, how do you define the overall energy of that particle? You will say, that will be the summation of the kinetic energy and the potential energy and then you will have some variables that you will solve for a given particle in classical mechanics.

In the case of quantum mechanics, we have what is known as the operators. This operator then operates on a certain function which in this case is the wave function. So, if it is a time-independent Schrödinger equation, in that case, the Hamiltonian operator will give you some values which are the values of energy. And these values are basically the orbitals. So, these are basically nothing but discrete levels of energy.

So, this is something you need to understand that orbital is not a physical thing. It is not a given path. It is just a level of energy that is where we have the highest probability of finding our electron. So, E here is the Eigenvalue. The eigenvalue is basically the most probable or most likely value of something. So, the Eigenvalue of energy will give you basically the shapes of the orbitals.

This is how we find out the shapes of the orbitals. One more important thing that you need to understand is that we are always solving the Schrödinger equation only for the hydrogen atom. A hydrogen atom has 1 electron. So, we are only solving it for 1 electron systems and not for multi-electron systems. So, all these orbital shapes are derived by solving the time-independent Schrödinger equation for the hydrogen atom. We do not consider the multiple interactions between multiple electrons. In fact, that is the reason we are solving it for a single electron system.

One more interesting and important thing for you to understand is that orbitals are discrete probability functions. When I say discrete, that means in one orbital the overall probability of finding an electron will be 1. Also in another orbital, the integral of probability will be 1. So, these are individual discrete probability density functions.

What is a free electron? Free electron is the electron that has zero probability of being found in any of the orbitals that participate in bonding. So, if there is an orbital that is not participating in bonding which means there is a certain energy level that is available for the electron. The electron can most likely be present there, but it will not participate in bonding and hybridization, which only takes place at the time of bonding or between the electrons which are participating in bonding.

So, if there is some unhybridized orbital in your system, in that case, the electron stays only in that unhybridized orbital and has zero probability of being found in any of the hybrid orbitals. That electron will be called the free electron.

Now you must have seen these kinds of diagrams. So, if I draw a p orbital, I will also draw it like that in this particular course (refer to slides). Again because this is just an easy representation, making two lobes.

As I said if I perform any experiment and I make a mark or I make a dot every time I find the electron, then ultimately if I do this a large number of times, in that case, this is the kind of image I will get and that is what the orbital would look like, but for easy explanation purposes even I will be using these kind of drawings.

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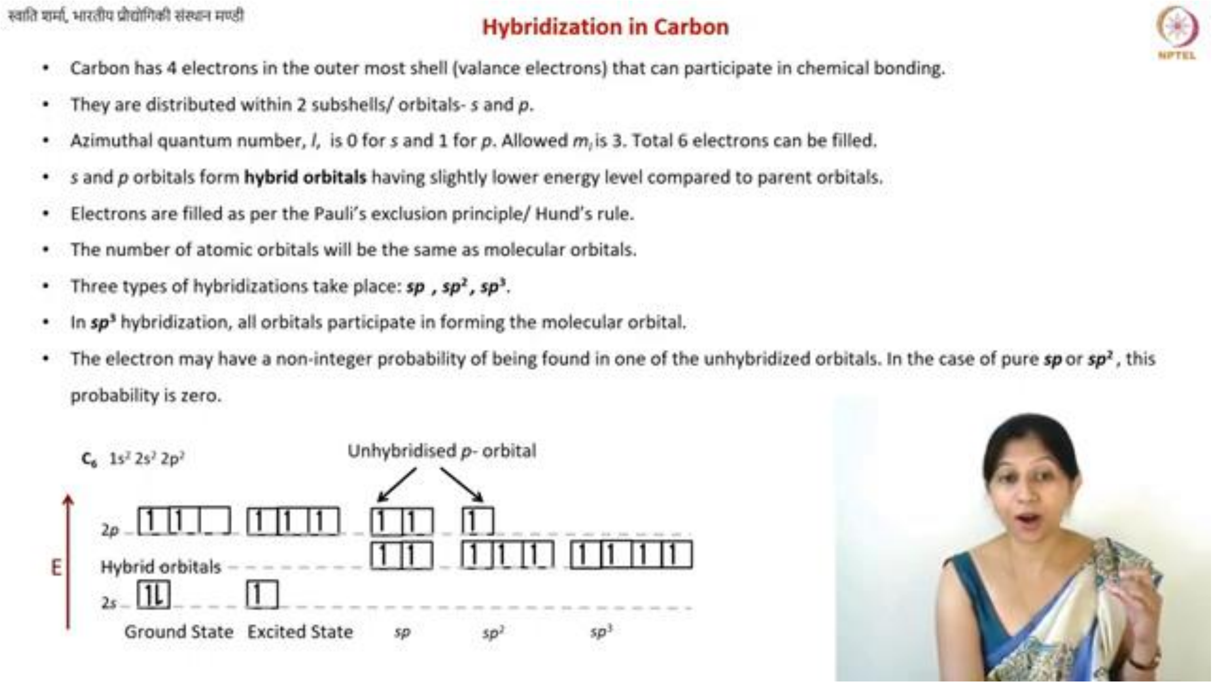

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Hybridization in Carbon

- Carbon has 4 electrons in the outer most shell (valance electrons) that can participate in chemical bonding.
- They are distributed within 2 subshells/ orbitals- *s* and *p*.
- Azimuthal quantum number, *l*, is 0 for *s* and 1 for *p*. Allowed m_l is 3. Total 6 electrons can be filled.
- *s* and *p* orbitals form **hybrid orbitals** having slightly lower energy level compared to parent orbitals.
- Electrons are filled as per the Pauli's exclusion principle/ Hund's rule.
- The number of atomic orbitals will be the same as molecular orbitals.
- Three types of hybridizations take place: ***sp*** , ***sp***^{2}, ***sp***^{3}.
- In ***sp***^{3} hybridization, all orbitals participate in forming the molecular orbital.
- The electron may have a non-integer probability of being found in one of the unhybridized orbitals. In the case of pure ***sp*** or ***sp***^{2}, this probability is zero.

Now let us talk about the hybridization specific to carbon. How many electrons do we have in a carbon atom? You know that we have altogether 6 electrons, but 2 of them are in the 1s shell. So, they are not in the valence shell. We do not at this point talk about them, we only talk about the 4 electrons which are in the valence or the outermost shell.

In this outermost shell, the principal quantum number or ‘n’ equals 2 and then there are 2 sub-shells. We have s-type of orbitals and we have p-type of orbitals. So, the azimuthal quantum number or ‘l’ is 0 for s and 1 for p orbitals. The allowed values of m_l for the p orbitals are +3 -1 0 and +1. We can have three types of p orbitals p_x, p_y and p_z. So, altogether how many electrons you can fill? You can fill 6 electrons. These 6 electrons can also come from another atom. So, this is what we have for carbon.

What happens At the time of bonding? Let us say I have one carbon atom and another carbon atom or another heteroatom comes close to it. The s and p orbital of a given carbon atom merge their energy levels and form the hybrid energy level and these hybrid energy levels are call hybrid orbitals.

Now we have the molecular orbitals formed with hybrid energy levels and these energy levels are slightly lower than the energy level of the p orbital. Now, I am going to describe that with this diagram. What do you see here? So, E is the energy. In the case of ground state carbon atom, you have this two s and two p orbital. There is a slight difference between the energy levels of s and p orbital of course. Now, when it is excited state, means this is the state when your carbon atom will have only when there is a possibility of bonding. So, in the ground state, you see that 2s orbital had two electrons and the 2p orbital also had two unpaired electron. But the third p_z type of orbital has no electron available. Now, in the excited state one electron because the difference of the energy of these two orbitals is not that high. So, in the excited state 1 electron from the from 2s orbital goes into the $2p_z$ orbital.

Now what happens during hybridization? Now, the orbitals with 4 unpaired electrons form a certain hybrid energy level which is the hybrid orbital, which you can see in the middle. In the case of sp, you have one s and one p orbital which go into this hybrid energy level. In the case of sp^2, you have one s and two p orbitals which will form the hybrid orbital. And in the case of sp^3, all four orbitals will participate. So, one s and the three p orbital will find a form 4 molecular orbitals which have slightly lower energy than the p orbital that we have in the beginning. So, this is basically the idea of hybridization.

Again this might be something that you already understand, but it is important because you will see in the next couple of lectures that the shapes of these hybridized structures or molecular orbitals after bonding whatever is formed at atomic or molecular levels, will define the crystal structure at a larger scale.

And the sp^2 type of carbon materials which are very interesting for us. Here you should already see that there is one unhybridized p orbital and this unhybridized orbital is responsible for all the interesting properties of graphite-like carbon materials, even including graphene which is the single layer of graphite. All the interesting properties are because of this unhybridized p orbital. In the case of sp, you will see that there are two unhybridized p orbitals. So, we should have even many more interesting properties. Well, sp hybridization is more common in the case of compounds rather than elemental carbon. Although there is one certain form of elemental carbon which has sp type of hybridization. This is something we are going to discuss in the next couple of lectures ok.

Now, how do we fill the electrons? Again their standard you know rules, for example, Pauli's exclusion principle or Hund's rule. All of these remain valid and then once we have the hybrid orbitals, we fill the electrons using the normal standard rules.

Importantly the number of atomic orbitals will be equal to the number of molecular orbitals. So, you cannot have 5 or 6 hybrid orbitals just by using one s and two p. So, here I have only shown the three primary hybridization states of carbon atoms. Why do I say primary?

Well, these are the only three possibilities. If think that orbital has to be an integer because as I mentioned the overall probability of finding an electron in the orbital will be 1. So, as such the orbital should be an integer, it cannot be a fraction. However, the probability of finding the electron inside an orbital can be a fraction because probabilities can be fractions.

This is something that is very important for you to understand because there is a possibility in the case of carbon of finding certain geometries which would only be possible if the hybridization state was between sp^2 and sp^3 or in some cases between sp and sp^2.

If you have certain geometry that is between sp^2 and sp^3, then if you back-calculate the hybridization, you will get something like sp^{2+n}. And this is very important for us that we are going to learn in this course. This is extremely important when it comes to the manufacturability of carbon.

Because you often find these kinds of structures at least in the large-scale carbon materials which are neither graphite-like nor diamond-like, but they are somewhere in between. And also then it becomes very difficult to understand them. These are the kind of structures that lead to the disorderness in carbon. And that is the reason, carbon are not completely amorphous because we will find some sort of crystallinity at all points.

So, it is very important to understand that although the orbital itself is a well-defined energy level. So, you can think of it in terms of an integer, but the probability of finding an electron does not need to be an integer because probability can be a fraction.

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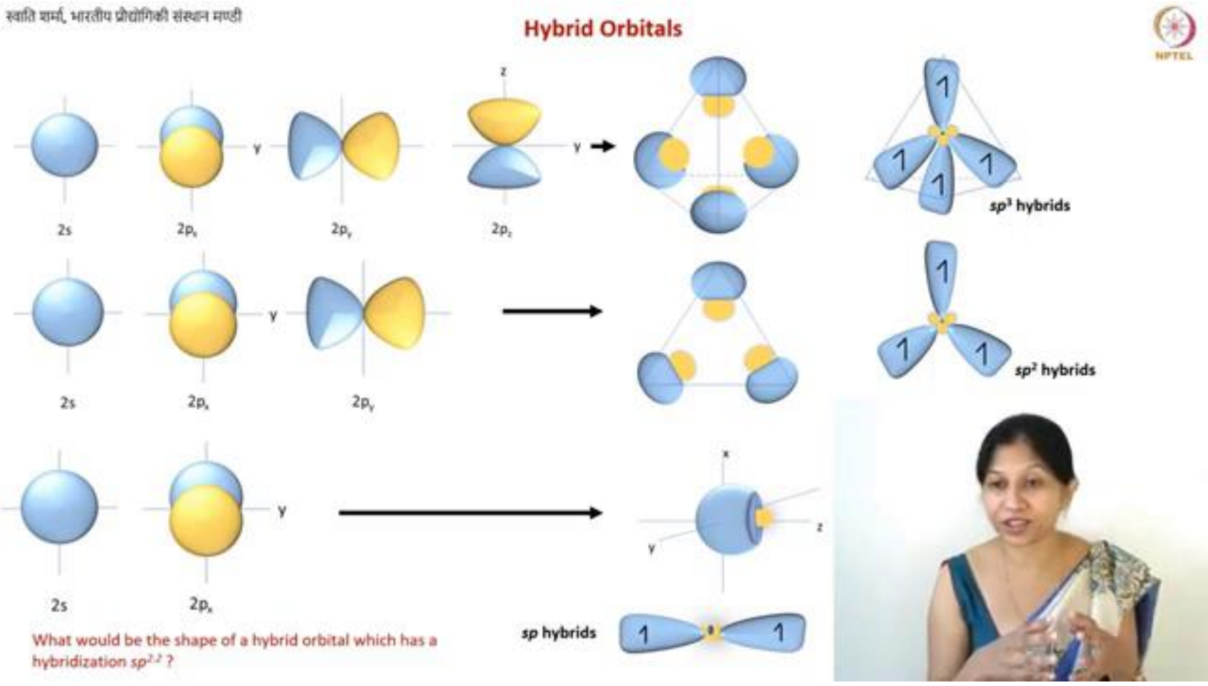

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Hybrid Orbitals

What would be the shape of a hybrid orbital which has a hybridization $sp^{2.2}$?

I already mentioned that these kind of images are just for easy representation. So, I am using these kind of images just to tell you the shape of your 2s, $2p_x$ and $2p_y$ and $2p_z$ orbitals. These kind of lobes can be found in these orbitals. And when we have the hybridized orbitals, then also we have certain shapes and these shapes basically will ultimately define your large scale crystal structure.

So, again I am using these kind of diagrams. I am showing you sp3 type hybridization first, So, once you have the hybridization, then what happens? The new hybrid energy levels that are formed when these energy levels merge have their the probability distributions in such a way that you get a tetrahedral kind of structure. This is what is known as a tetrahedral structure.

Again so, there are certain regions where you see that some lobes have a higher probability and the other lobe has become smaller. There is no change in the physical shape or anything, these are just the probability distributions.

Now, there is a higher probability that you will find electrons away from each other. Because when you have the electrons, then they are always trying to move away from each other after bonding. So, now, when you have two sp^3 type carbon atoms bond together. So, 4 electrons of 1 atom and 4 electrons of the second atom, they go into these four molecular orbitals which are your hybrid orbitals. Now, all of these electrons want to move apart from each other. They want to go as far as possible from each other and in that case this particular geometry is the most suitable geometry for them. Another slightly different representation would look like this. These are the sp^3 hybridized orbitals. Often you will hear that either the word tetrahedral or pyramid shape. Let us say if the electrons are sitting at the end of these the lobes that I have shown, if you connect them, then you will get this pyramid like geometry. This is the geometry of diamond type carbon.

Here I have only one set of hybrid orbital and this only happens at the time of bonding. You will have another hybrid orbitals like this. And I have only shown the 4 electrons of two similar hybridized orbital, all the electrons will get paired up and there will be bonding.

All of these bonds will then be sigma type of bonds and that is why diamond has a very strong geometry and it also has very strong bonding and no free electron available for electrical conductivity. And at a larger scale the diamond crystal structure has these pyramid like shapes and that is why when we cut the diamond, we get these you know different facets. So, this is how your sp^3 type hybridized orbital look.

What happens in the case of sp^2 hybridization? Now, you have one s orbital, two p orbitals and the third one is unhybridized, it does not participate in hybridization. In that case, you have this kind of shape (refer to slides). Now for three hybrid orbitals, if they want to move as far from each other as possible, the optimum geometry is a planar geometry. So, you have a plane triangle and all three corners will you know again for an easy representation will contain the electron. The electrons can now move as far from each other as possible.

Again if I take one such sp^2 hybrid orbital, then it will look like this. Basically these kind of geometries are known as trigonal planar geometries. Now, I have not shown the unhybridized orbital here.

What happens in the case of sp hybridization? You only have one s and one p, which basically will give you a linear type of shape. So, again because there is only one such orbital shown here, then you see only half of this shape, another half will be you know completed by another neighboring atom and what you will have is a linear type of final geometry of the molecule. So, these are three different types or different shapes of hybridized carbon atoms and this will defining all of the properties of carbon materials at a larger scale.

So, this is the geometry which I have shown, which basically tells you how the molecule will look like. Now, we are going to discuss this after one or two lectures. Some of these are the shapes of the sp^2 sp^3 sp hybridized orbitals.

But if I give you some random number, let us say $sp^{2.2}$, can you think of what is the geometry? What will it look like? $sp^{2.2}$ means it should be between diamond and graphite, but between diamond and graphite, think of a geometry that your hybridized orbitals can adopt.