Introductory Organic Chemistry

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Lecture 02
Introduction to Molecular Orbital Theory Part - 1

So welcome. Today we are going to talk about Molecular Orbital Theory, but before we go to molecular orbitals let us revise what atomic orbitals are? So, in the last class we talked about atomic orbitals and we said that they are really a region around the nucleus or region in three-dimensional space around the nucleus, where the probability of finding an electron is the highest. Using various computational tools and mathematical tools, we have figured out that each of these orbitals have designated shapes and size. The s orbital is defined as a spherical orbital and you can never really say where exactly an electron is in this space, but we say that the probability of finding an electron in the space is the highest.

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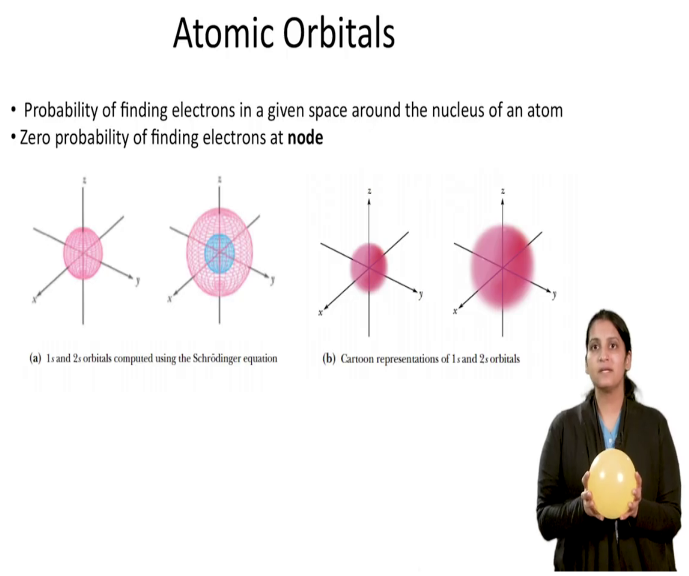

Atomic Orbitals

- Probability of finding electrons in a given space around the nucleus of an atom
- Zero probability of finding electrons at **node**

(a) 1s and 2s orbitals computed using the Schrödinger equation

(b) Cartoon representations of 1s and 2s orbitals

So, 1s orbital is spherical, 2s orbital is also spherical, but distance from the nucleus for the 2s orbital is much higher than for the 1s orbital. As you can see here we have shown the shapes of 1s and 2s orbitals using Schrodinger equation and also some computer cartoon representation of these 1s and 2s orbitals. The 2s orbital as you can see has a node in between and the probability of finding an electron in this particular node is zero; there is no node for the 1s orbital.

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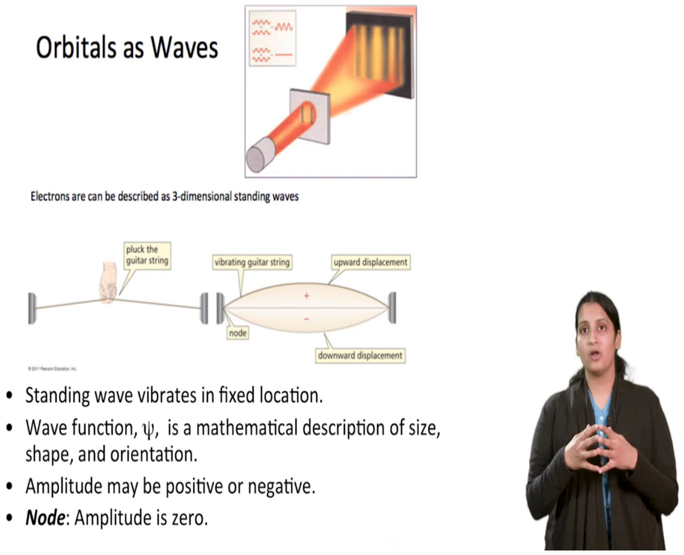

Orbitals as Waves

Electrons are can be described as 3-dimensional standing waves

- Standing wave vibrates in fixed location.
- Wave function, ψ, is a mathematical description of size, shape, and orientation.
- Amplitude may be positive or negative.
- ***Node***: Amplitude is zero.

In order to understand the molecular orbital theory, we need to think of orbitals as waves because electrons can be thought of as standing waves, right. So, electrons have a particle nature and they also have a wave like nature and we have to think of electrons as standing waves for molecular orbital theory. So, standing waves vibrate in a fixed location, so you can think of it as a guitar string that is vibrating up and down. So, you can see that the amplitude can go up and down and really can have two phases as positive and negative. And in our case, we are going to represent a wave function psi which is a mathematical description of the size, shape and orientation of this particular wave.

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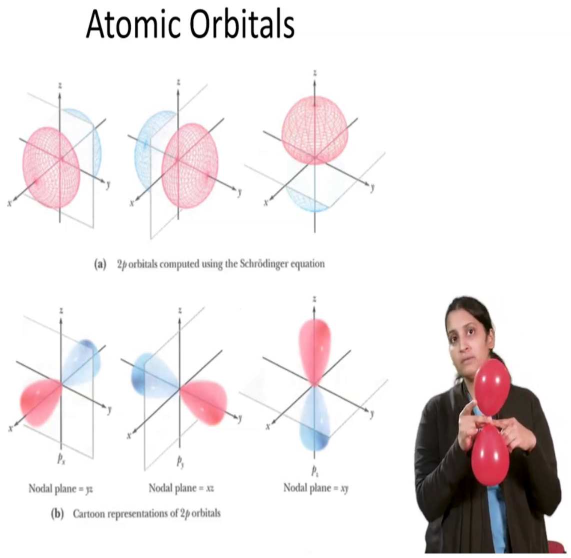

Atomic Orbitals

(a) 2p orbitals computed using the Schrödinger equation

Nodal plane = yz

Nodal plane = xz

Nodal plane = xy

(b) Cartoon representations of 2p orbitals

So, we talked about s atomic orbitals. Let us also talk about the p atomic orbital and p atomic orbital as we described in the last class has a dumbbell like shape meaning it has two lobes. They are typically represented, their phases are represented using a sign positive and negative, but remember the electron can be anywhere in this entire p orbital and there are three p orbitals. There is a px orbital which is symmetrical around the x axis, then there is py orbital which is symmetrical around the y axis and you also have a pz orbital which is symmetrical around the z axis. There is one node to this p orbital where the probability of finding an electron is zero.

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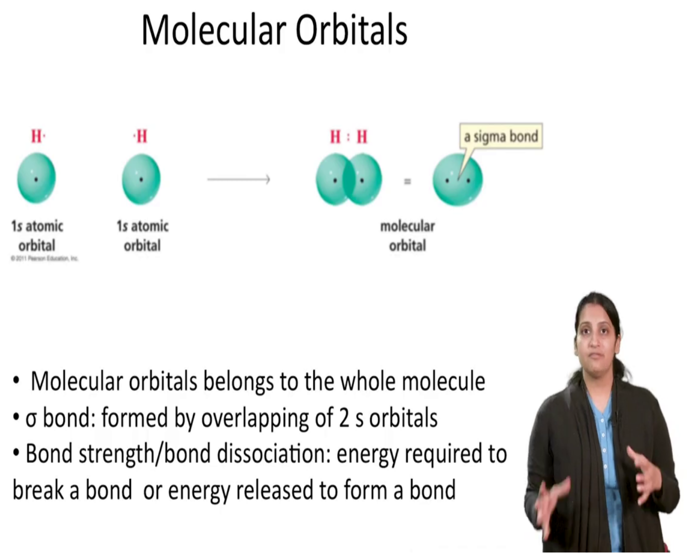

Molecular Orbitals

- Molecular orbitals belongs to the whole molecule
- σ bond: formed by overlapping of 2 s orbitals
- Bond strength/bond dissociation: energy required to break a bond or energy released to form a bond

So, when we start talking about molecular orbitals, we have to understand that molecular orbitals result as a combination of atomic orbitals rather when n atomic orbitals combine, they form n molecular orbitals. This is something we want to remember. So, n atomic orbitals give rise to n molecular orbitals. So, in the case of hydrogen atom, you have one atomic orbital which is the 1s orbital, but when a hydrogen molecule is formed which is H2, you have two atomic orbitals each from one of the hydrogen atoms combining to form to molecular orbitals.

So, now let us look at this particular combination and understand the formation of hydrogen molecule. So, what we are saying is that 1s orbital of one of the hydrogen atoms and the other 1s orbital of the other hydrogen atom is going to combine and really form, together it is going to form a molecular orbital. And as you can see on screen, we have represented this using this diagram where in now we have formed a sigma bond between the two hydrogen atoms.

So, one thing to remember is that the molecular orbitals belong to the whole molecule and not to an individual hydrogen atoms. So, now once the molecular orbitals are formed, they belong to the whole hydrogen molecule and sigma bond results because of an overlap of these two atomic orbitals. So, when two atomic orbitals combine and overlap such that there is a maximum overlap possible, this results in the formation of sigma bond.

Last class we also talked about bond dissociation energy which was the energy that was required to break a bond apart. So, let us say I have to break these two hydrogen atoms apart from each other. I will require an energy corresponding to bond dissociation energy and once that energy is provided, those two hydrogen atoms can be taken apart from each other from that hydrogen molecule.

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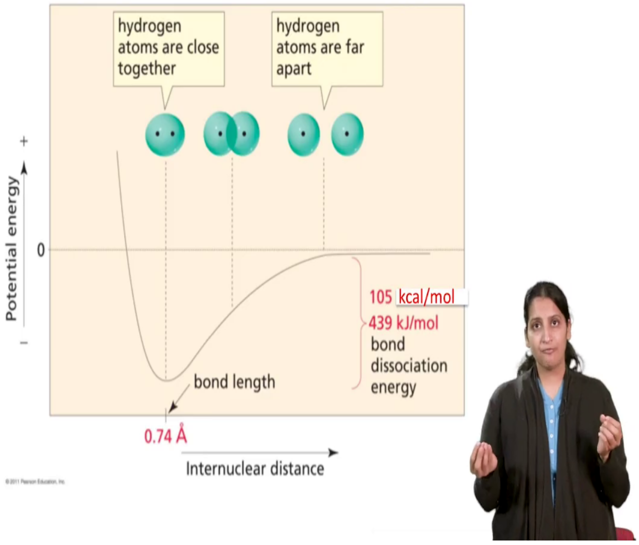

So, now let us think of this particular formation of hydrogen molecule. Imagine that these two hydrogen atoms are standalone. They each have their 1s orbital and they are starting to come close to each other. So, as you can see as this distance between the two hydrogen atoms goes on decreasing, you start having an overlap. So, in this case for example, you will slowly start having an overlap between the two 1s orbitals and as this distance goes on decreasing, what happens is that at a particular distance you have maximum overlap and that is in fact the bond length of the hydrogen molecule or the bond length of the hydrogen - hydrogen bond. This particular distance or bond length also results in maximum stabilization.

So, you can see that the potential energy is minimum at the bond length. So, last class we talked about the numbers and hydrogen - hydrogen bond is approximately 0.74 Angstrom or 75 picometers and at this particular distance you have maximum stabilization. So, this stabilization is equivalent to 105 kilo calories per mole of energy.

So, as two atoms come closer and they get stabilized, the energy is released and this energy is corresponding to 105 kilo calories per mole. If I bring these atoms even more closer such that they are now beyond the bond length, I am trying to get them closer then remember that the protons in each of these atoms or nucleis of this atom, they are going to start repelling each other because the positive charges are going to repel each other. So, if I want to go beyond the bond length and get these atoms close to each other the energy, the potential energy is going to increase tremendously and that is what this graph represents.

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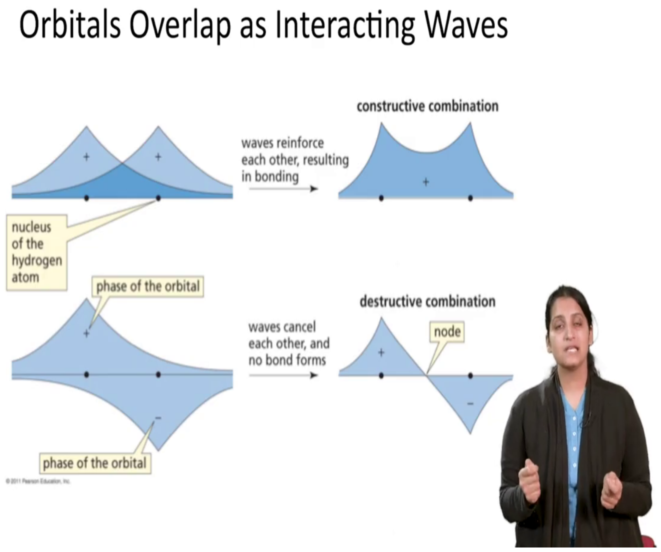

Orbitals Overlap as Interacting Waves

So, we talked about how orbitals are like waves or standing waves and we have to also think of this orbital overlap. So, in the case of hydrogen - hydrogen atom, the orbitals were overlapping, right.

So, in this case we also have to think about this orbital overlap like a wave overlap. So, imagine two waves going and combining together. Now, there are two ways of combining either such that the two waves have a synchronous addition in the sense that the crest of one wave matches with the crest of the other wave and they both add together or you can have an asynchronous addition, wherein the crest of one wave matches with the trough of the other wave and they basically cancel each other out. So, there are two ways of adding two waves using a synchronous and asynchronous addition.

So, as you can see here this particular diagram represents the orbital overlap as interacting waves. So, a constructive combination or a synchronous addition results in a large trough or adding two waves together and a destructive combination results in two wave subtracting from each other and in fact, you have a node here when the combination results in a destructive way.

So, we say that the bond is formed when these two waves add in a constructive manner and the bond is not formed or, there is no bond formation when they add in a destructive manner.

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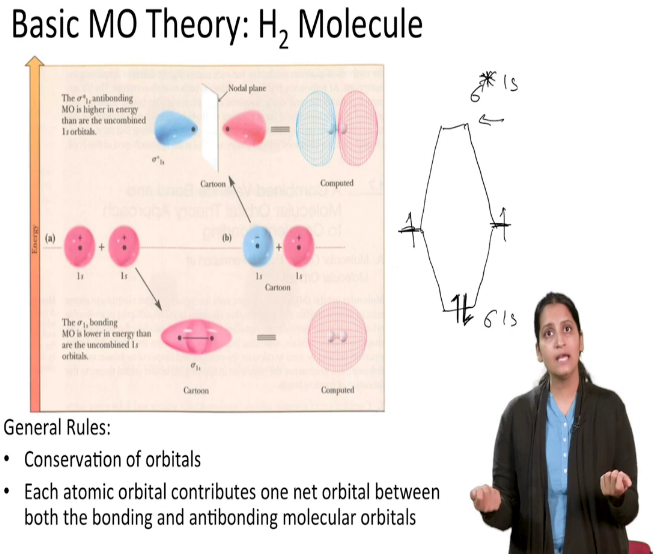

Basic MO Theory: H_2 Molecule

General Rules:

- Conservation of orbitals
- Each atomic orbital contributes one net orbital between both the bonding and antibonding molecular orbitals

So, now let us look at this hydrogen molecule formation. Imagine that in one case these two 1s orbitals are adding such that they are adding in a constructive manner which results in release of energy and stabilization. You can see that this particular orbital diagram or molecular orbital diagram is typically made where in the two atomic orbitals are combined.

So, you can see that you represent addition of these two atomic orbital such that it results in a constructive combination, such that the energy is lower than the energies of corresponding atomic orbitals, or you can have a destructive addition where the energy is higher than the energy of the corresponding atomic orbitals. So, two atomic orbital combined to form two molecular orbitals and we say that the two atomic orbitals have now combined to form a sigma 1s orbital and then sigma star 1s orbitals.

So, it is also termed as, sigma 1s is the bonding molecular orbital and sigma star 1s is the antibonding molecular orbital. You can see the shapes of these two represented on the screen. Now once we have designated these molecular orbitals, we go on filling electrons into these molecular orbitals just using above principle and Pauli's exclusion principle. So, what we are going to do is, we are going to take 1-1 electron from each of these hydrogen atoms. Now, we have two electrons and we have to place them in these molecular orbitals.

So, what I am going to do is, I will fill these two electrons in the lower most energy orbital which is the bonding molecular orbital and they have to be paired with each other using Pauli's exclusion principle. Now, I am done with adding two electrons. So I have no more electrons left to put in the sigma star molecular orbital or the antibonding orbital. Molecular orbital theory can also tell us which bonds are going to result in a stable bond formation. For any bond to be stable, you need to have more electrons in the bonding molecular orbital than in the antibonding molecular orbital.

So, for example hydrogen molecule exists because you have more electrons in the bonding molecular orbital and the antibonding orbital is empty. If you take helium; so, if I try to combine two helium atoms, each of the helium is going to come with two electrons. So, if I now have to make a similar diagram for helium, you can imagine that the bonding molecular orbital will have two electrons in it, the antibonding molecular orbital will also have two electrons in it.

So, this does not favor stability. You need to have more electrons in the bonding molecular orbital. So, as a result of which helium as we know does not form a molecule of He2 just like hydrogen forms H 2. You do not have helium forming He2 and you can also predict for many other atoms whether a particular atom is going to form a molecule using the Molecular orbital theory.

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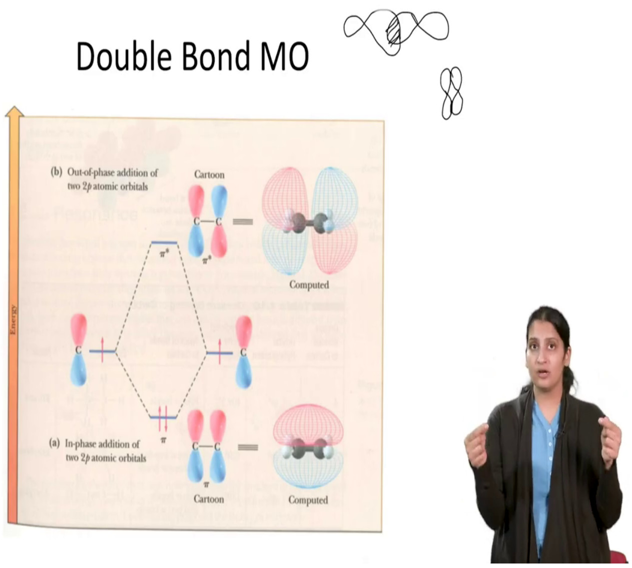

Double Bond MO

So, we just looked at a single bond formation. Now, let us look at 2p orbitals overlapping with each other. Now, there are two ways in which I can think of these two particular p orbitals overlapping with each other. I can think of an end to end overlap such that these two orbitals now overlap with each other or I can think of a side to side overlap wherein you have these two orbitals overlapping with each other.

If I have to represent it in a diagram, I would say an end to end overlap is something like this wherein you have a large overlap or large portion of overlap happening between the 2p orbitals or you can think of a side to side overlap wherein the overlap is not that effective. Whenever you have an end to end overlap, that overlap results in the formation of a sigma bond. Whenever you have a side to side overlap, that particular overlap typically results in the formation of a pi bond.

So, now let us look at this pi bond formation or double bond formation. So, now what I have is a carbon - carbon double bond forming. Now, each of these carbon in the p orbital has 1-1 electron. Each of these p orbitals from carbons are going to combine to give you one molecular orbital which is represented by pi molecular orbital and you are also going to get a corresponding pi star molecular orbital. So, n atomic orbitals give rise to n molecular orbitals. So, if I combine 1 p orbital from each of these carbons, I am going to get one molecular orbital which is a pi molecular orbital and one pi star molecular orbital which is the antibonding orbital.

So, as you can see if I go on filling for a carbon - carbon double bond, I have two electrons. So, they go in the pi molecular orbital. I do not have any more electrons remaining. So, there is nothing to be placed in the pi star molecular orbital and the carbon - carbon double bond can be considered as a stable bond.

So, we know that carbon forms four equivalent bonds. In the case of let us say compound like methane, you have four equivalent bonds between carbon and hydrogen, but if we look at the electronic configuration of carbon, it is not really straight forward as to how carbon is able to form these bonds equivalently such that they are equal in their shape, size, energy and so on.

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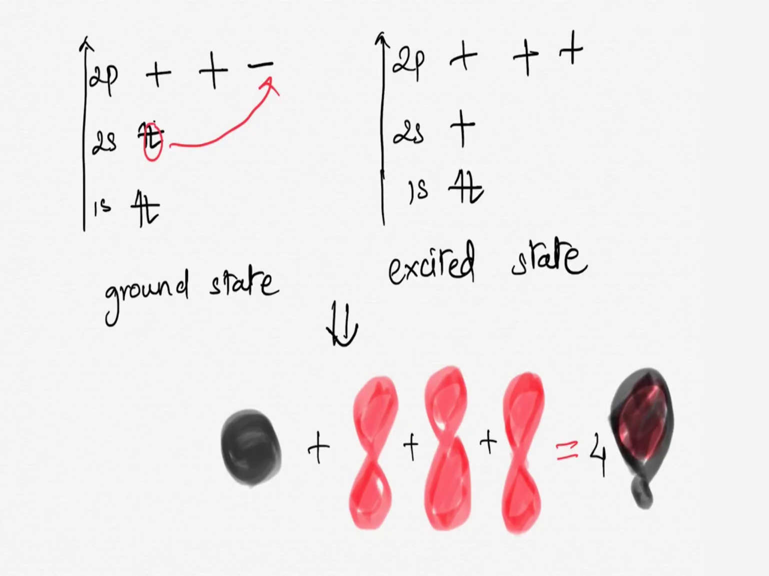

So, let us first revise the electronic configuration of carbon. We said that ground state electronic configuration of carbon is 1s 2, 2s 2 and then 2px1 and 2 py1 and then, the 2pz 1; z orbital is really empty. So, if you really look at this particular diagram, it does not really represent how carbon is able to form four bonds because in order to form four bonds, you need to have four orbitals that are overlapping with each other. Not only that the current state in which the electronic configuration is written, you cannot have four orbitals in which you can form four equivalent bonds.

So, in order to explain the bond formation in methane, scientists came up with a concept of hybridization. So, hybridization is when you combine two orbitals to make one hybridized orbital. Now, in the case of carbon what happens is that you have the ground state electronic configuration. This particular ground state electronic configuration is revised to form an excited state electronic configuration. So, this is ground state and we are going to draw an excited state electronic configuration wherein one of these electrons from this 2s orbital has been put into the 2pz orbital.

So, now the excited state electronic configuration becomes 1s 2, 2s 1, 2px1, 2py1, 2pz1. In this particular configuration as well you cannot explain the bond formation wherein four equivalent bonds are formed. You can certainly explain how four bonds will be formed, but remember the bond that is formed with this electron that is in 2s orbital will be different from the bond that is formed with the electron in the 2p orbital.

So, in order to explain this equivalent bond formation what chemists came up was the hybridized state or hybridized state electronic configuration. So, I am going to draw the hybridized state. Now, when we draw the hybridized state what we are going to do is, we are going to combine that one electron from the 2s orbital and then the three electrons from the three of the p orbitals getting them together and combining this one of the s orbitals and three of the p orbitals to give rise to sp3 hybridized orbitals.

So, I am going to draw it such that; imagine that you are combining one of these s orbitals and then, I am also combining three of these p orbitals together. You can imagine this is pretty much like taking an apple and 3 oranges and mixing them in a blender and then coming up with four glasses of apple orange juice, right. So, what I have is now no longer the addition.

Once I do the addition, it no longer represents s orbital or p orbital. Rather what I have is a combination of both of these orbitals and this results in the formation of sp3 hybridized orbital. So, I am going to say that this addition gives me what I call as the sp3 hybridized orbital. I am also going to show both the colors because that is how it is, right. So, when I add these things together, the s lobe can be added to the p lobe or s lobe can be subtracted from the p lobe.

So, what I have here is a kind of a distorted dumbbell shape wherein you have one large lobe and one tiny lobe. So, as I add one of this acentric of the piece, I do not result with just one sp3 hybridized orbital, but remember the law that n atomic orbital will give rise to n molecular orbital. Similarly, here when four orbitals are combined, we give rise to four of the sp3 hybridized orbitals.

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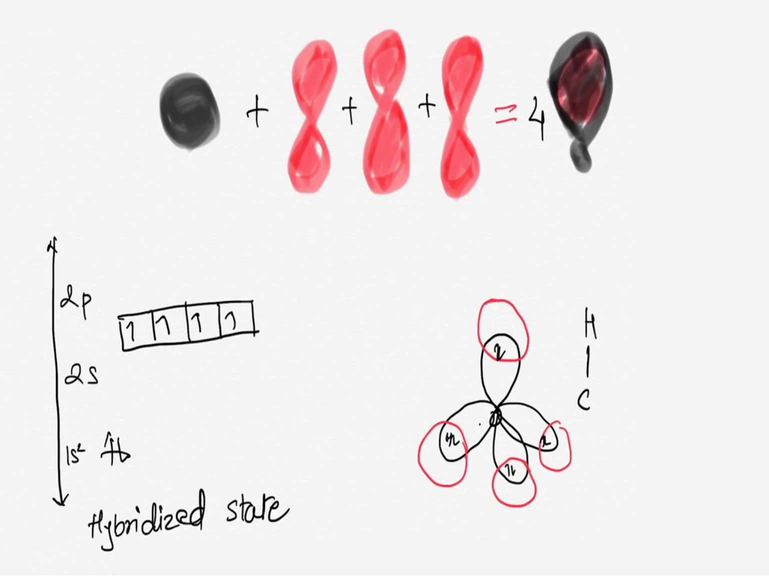

So, I am going to draw this diagram wherein 1s and 3p give rise to four sp3 hybridized orbital. Now in order to represent it in the electronic configuration what I am going to do is, you have 1s2, you have 2s and 2p and the energy of the sp3 hybridized orbital is going to be in between s and p hybridized orbitals, but it is going to be closer to the p atomic orbitals because remember if you have a larger p contribution, then the energy of the hybridized orbitals is going to be closer to that of the p orbital.

So, now I am going to draw the hybridized orbital. So, I have formed four of them and in each one of these hybridized orbital, there is 1-1 electron each, okay. So, the hybridized electronic configuration or hybridized state electronic configuration is represented as follows. Now, you can imagine that since I have four equivalent hybridized orbitals around this carbon atom when it forms bonds, it is going to form four equivalent bonds. So, in order to represent that I am going to use these as my hybridized orbitals, okay.

So, as you can see in order for me to hold these four orbitals such that they are stable or farthest away from each other, what I give rise to is a shape closer to that of a tetrahedron. In fact, the Valence Shell Electron Pair Repulsion theory or VSEPR theory says that these hybridized orbitals have to be oriented such that they are farthest apart from each other. So, when I have four of these hybridized orbitals, the only way to orient them is using in a tetrahedral fashion or something like this, okay. So, imagine that the carbon has this particular hybridized state electronic configuration wherein there is 1-1 electron in each of these lobes and then hydrogen in its 1s orbital is going to come and overlap between sp3 hybridized orbital of the carbon and 1s orbital of hydrogen and when you have this overlap, there is a carbon hydrogen bond formed.

So, in order to show it what I am going to do is, I am going to draw this sp3 hybridized orbital and then, the 1s orbital of the hydrogen is going to overlap like this. So, this is one of the carbon hydrogen bonds. Similarly, I am going to have four of these carbon hydrogen bonds. So, you can imagine that there will be a corresponding overlap and this electron pair get shared such that you have a covalent bond formation, right. So, one of the electron comes from hydrogen, the other electron comes from the carbon and both of them share this to form a covalent bond between each other. Herein I have a ball and stick model of a methane molecules.

So, you can see that the central carbon atom has formed bonds with four of the hydrogen atoms and now you have what is called as the methane molecule. In this particular methane molecule since we want to follow the valence shell electron pair repulsion theory, you what you can see is that they are, the two, the orbitals are farthest away from each other and the bond angle between these two bonds becomes 109.5 degrees. So, for sp3 hybridization, the bond angle is typically 109.5 degrees. Okay, so we just talked about the hybridization of carbon in methane and in fact, this is kind of the model in which the four sp3 hybridized orbitals of carbon are centered.

So, we can imagine that the carbon nucleus is kind of, in the centre and these are the four orbitals in which the electrons are placed and each of these orbitals will overlap with 1s orbital of hydrogen to form the bonding in methane. Now, how does this bonding change as we go from carbon to nitrogen to oxygen?

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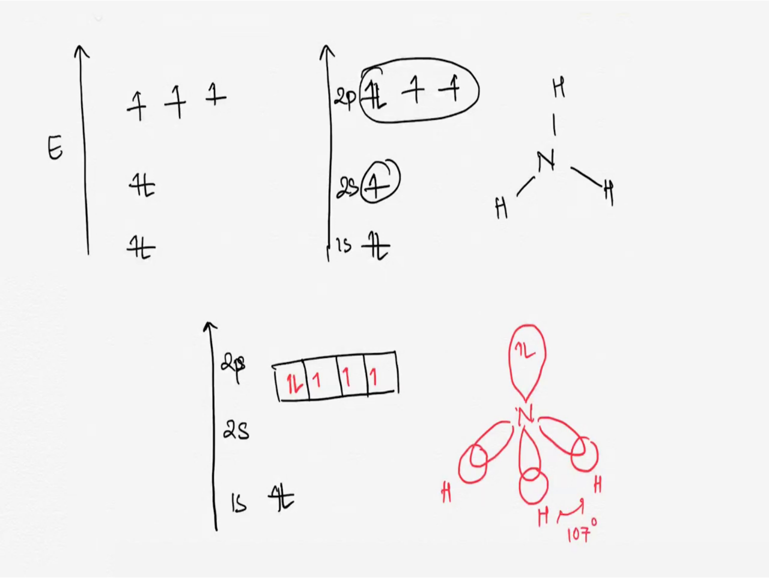

So, now let us look at some of the examples of sp3 hybridized nitrogen and sp3 hybridized oxygen molecules. So, the first example we are going to take is ammonia. Now, the ground state electronic configuration of nitrogen is what I have shown here and as we said that in order to go from ground state to hybridized state, we need to first go through an excited state. So, in this case I am going to make one of this 2s electrons jump from the 2s orbital to the 2p orbitals. So now, what I have is this is the electronic configuration of the excited state of nitrogen. In order to draw the sp3 hybridization of nitrogen, I need to take one of the s orbitals and three of the p orbitals together.

So, I am going to take the 2s and then, these three 2p orbitals combine them together, kind of mash them in a blender and come up with four sp3 hybridized orbitals. So, now what I am going to draw here is the hybridized state electronic configuration of nitrogen. So, I have 1s orbital completely filled and then, between 2s and 2p orbitals, now what I have is four of these sp3 hybridized orbitals. They are same in their shape, size, energy and now in these four orbitals I have total 5 electrons to place.

So, that is what I am going to do. I am going to place them such that they look like this, right. Now, if you think one of the orbitals is completely filled and three of the other orbitals are half-filled, so these three orbitals are going to overlap with each of the hydrogens in the case of ammonia to form bond between nitrogen and hydrogen. So, in the case of ammonia, what happens is, each of the half filled orbitals that is sp3 hybridized will overlap with the 1s orbital of hydrogen and in fact, one of the orbitals which is sp3 hybridized has a completely full orbital, that is, both the electrons are present and that is the lone pair in the case of ammonia.

So, how does this change the geometry? We talked about the bond angle being 109 degrees. So, in fact what happens is, the lone pair, let’s imagine that this is the nitrogen and these are the four sp3 hybridized orbitals. The lone pair here is going to occupy more space around the nitrogen atom that is because it’s going to repel the other electrons. So, there is a higher repulsion when a lone pair is present. So, it’s going to try and occupy space around here, kind of pushing these other bonds down. So, it kind of pushes them down.

So, what happens in a way is that you have a higher bond angle between the lone pair nitrogen and hydrogen and the bond angle between hydrogen, nitrogen and hydrogen kind of goes down. So, the bond angle was 109.5 degrees in the case of methane. In the case of ammonia that is going to go down and become close to 107 degrees, okay. So, the hybridization remains the same, but because you have a presence of a lone pair, the bond angles have changed a little bit and it gives a different geometry to the nitrogen atom. Same thing in the case of let’s say, let’s take the example of water.

Now, in water oxygen is going to be sp3 hybridized. So, you can actually do this exercise and try to write the excited state electronic configuration of oxygen and also write down the hybridized state electronic configuration of oxygen. So, as you do that you will realize that instead of now just one lone pair, the oxygen will have two lone pairs present.

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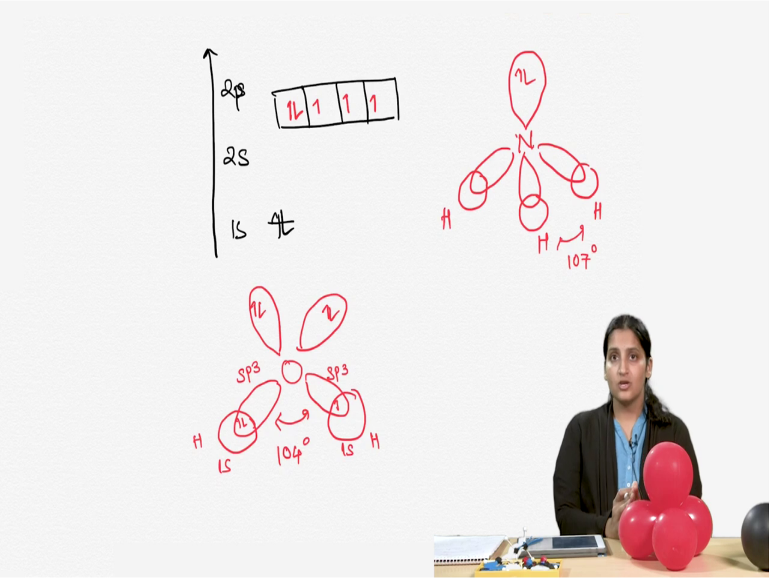

So, in the case of water the structure is like the central oxygen has two of these sp3 hybridized orbitals that are occupying 1-1 electron and they overlap with 1s orbital of hydrogen, okay. But oxygen also has, what it also has a two lone pair. So, there are two lone pairs present on that oxygen and because of which there is even more repulsion now. So, the bond angle in the case of water molecule goes down from even 107 degree and the hydrogen oxygen hydrogen bond angle in the case of water will be 104 degrees, approximately 104 degrees.

So, as you can see as the presence of lone pair increases on that central atom, the bond angle goes on decreasing in the case of sp3 hybridization.