

Lecture 11A • 02/13/12

Conjugation is really talking about distributed molecular orbitals, in which we represent those orbitals through the combination of a whole series of p orbitals. When we talked about bonding and antibonding, we talked about it being the overlap of different orbitals. You might remember a pi bond: we used two p orbitals in different ways to make both the pi bond and antibond. Well, now if you end up with a system where multiple p orbitals overlap, what we need to see is what is the effect on the set of molecular orbitals that's formed. It's just an extension of bonding and antibonding.

What is a bond? Why does a bond form? To release energy. A bond is something that happens because energy is released. There's the classic way of describing that, talking about plus charges and minus charges and how far away they are from each other. That classical view leaves out one really important point: that these charges are not particles; that they really act like waves. So, any description we have of bonding or antibonding, if we want to be complete about it, better include something to do with waves.

Do atom orbitals exist in a system that has bonds? No. Why not? You can solve the Schrödinger equation, the equation that actually gives you the functions that map out those different orbitals – you can solve those functions if you have one electron only in your atom. If you have multiple electrons, you can still come up with the orbitals, but you can't solve them directly, because there are too many variables involved. But they're still atomic orbitals. But if you have a bond, that means that you have more than one nucleus around. If you have more than one nucleus around, do you really still have atomic orbitals? Technically, no. If you think about what the s, p, d, and f orbitals look like, you've got the nucleus in the center here, an s orbital is symmetric around that; a p orbital is symmetric in that it's cut right in the middle (where the nucleus is). A d orbital's a flower shape that's still with the nucleus right in the middle. In other words, all of these shapes, all of these patterns, depend on the fact that you have one nucleus and however many other electrons around. As soon as you have multiple nuclei, that electron is going to be influenced by more than one nucleus. That means, automatically, the shape of the orbital you get is going to be different.

Sometimes, it's not that different. Sometimes, it's close enough that we use atomic orbitals to represent molecular orbitals. We even do that for bonds. A bond exists, no matter what our description of it is, but we have a way of describing it where we use atomic orbitals to get at bonds. Why? Because it takes an awful lot of math and concept just to understand an atomic orbital, and once you've done all of that work, do you want to throw all of that away? To get the exact right answer, the answer might be yes, but we can estimate what bonds look like by using atomic orbitals.

Atomic orbitals (AOs) describe the possible locations of electrons in a mononuclear system. All of the shapes of atomic orbitals depend on the presence of only one nucleus, and are all symmetric around that nucleus. Molecules have bonds, which are interactions between multiple nuclei. They're favorable – that's why they happen – but they're interactions between multiple nuclei. The shapes of the orbitals involved are automatically different because multiple nuclei are involved. Because multiple nuclei are involved, you can't directly use atomic orbitals to express what's going on in a molecule.

Methane demonstrates two problems: that if you look at the atomic orbitals in the valence shell of carbon, relative to each other, they all have 90° angles. But in methane, you've got 109.5° angle, it's a tetrahedron. Similarly, if you look at s and p orbitals of carbon, in a polyelectronic, not [poly]nuclear, system, where you do have electrons interacting with electrons, orbitals are no longer necessarily equal in energy. A 2s orbital in carbon is a different energy than a sp orbital; but in methane, you have four energetically-equivalent bonds. This is where hybridization comes from. Hybridization is a way of combining atomic orbitals in order to create a system of molecular orbitals that match the geometry of the molecule. That's not quite what bonding is, but that's where the store of methane comes from. [Hybridization] is one stepping stone leading up to bonding.

Hybridization is a process of combining atomic orbitals on the same atom to describe the structure of a molecule. Hybridization involves combining atomic orbitals to create, effectively, new molecular orbitals (MOs) that match the geometry of the system. I'll put in parentheses here – match VSEPR. VSEPR theory [is] this way of predicting what molecular structure's going to be by simply look at the number of pairs of electrons and how they would all repel each other. If that prediction normally holds true, then we have to back and say, how could we make atomic orbitals give us the same answer. That's what hybridization is. Notice that hybridization involves combining atomic orbitals on the same atom to create these hybrids. Bonding can be [represented] by combining atomic orbitals on different atoms. At this point I could talk about H₂ and He₂ and why hydrogen forms and helium doesn't. Then we could talk about oxygen, when we start involving both s and p orbitals. I want to have a more focused discussion of just the pi bond and, maybe if we have time, a sigma bond. What we're doing is leading up to conjugation, which is where you can have multiple p orbitals overlap each other.

I guess we better do a sigma bond so we know how to model a sigma bond. Instead of just doing plain old hydrogen, let's look at a bond in something like methane. This'll be another chance for me to review SMOGs – structural molecular orbital graphs – that we used to show what types of orbitals are present on a molecule. What's the hybridization of carbon in methane? Sp³.

SMOGs – structural molecular orbital graphs – a graphical depiction of the types of orbitals present in a molecule, ignoring sign of the wavefunction. [review of shading] We're going to be using two sets of diagrams: the SMOGs to just see the structure, but then a bonding diagram to show the types of interactions that are going on. SMOG diagram for methane would look pretty simple. A hybrid orbital technically has a node; this, for the moment, is a drawing that does show wavefunction sign. When I represent hybrids, I'm going to simplify, because that's not really drawn quite correctly; one half, or one segment, or lobe of that hybrid orbital is much larger than the other. There's enough difference where I simplify and just write one of the lobes. If I'm drawing methane, I'm going to draw the four sp^3 orbitals. Attached to each one of those is an s orbital. For methane, it's a pretty simple diagram. There's one key point here: notice that the sp^3 orbital is written as a distinct orbital from the s orbital – in other words, it's not just one blob that connects the two. But in reality, it is just a blob of electron density that's there; in methane, there is no sp^3 orbital or s orbital, it's four sigma bonds. But this is the way that the picture is drawn so that we can understand the structure, but this is not what it really is, this is our way to represent it.

Now let's focus on how would we represent that sigma bond that's here. It's a little more complicated than hydrogen, but let's tackle that. Here's one of the complications: in hydrogen, when we learned about making sigma bonds, we had two orbitals that were equal in energy, on hydrogen connecting to another. We now have an sp^3 orbital from carbon bonding with an s orbital from hydrogen. There's going to be differences in those orbital energies automatically, cause there's a different number of protons in the carbon versus hydrogen, but ignoring that, why do you think it is that an s orbital in general is lower than sp^3 in energy? It's closer to the nucleus. Why would the sp^3 be further from the nucleus? Because it has more what's called p-character. [We used the term] character when we were describing the acidity of alkanes, alkene versus alkynes. We also used an argument there about how the type of hybrid present would influence how acidic the compound is. The reasoning there was that, in an alkyne, if a hydrogen came off an alkyne, a negative charge is going into an sp orbital. Sp is only 50% p; p is higher than s, but that's better than if we have an sp^2 orbital, which is only a third s, versus an sp^3 orbital, which is only 25% s. The s there is, the higher energy it is, which is how we get to the same situation here. But, they are close enough in energy that they're going to still overlap with each other.

Automatically, there are two orbitals created when two nuclei interact. One is favorable, a lower energy than either orbital to begin with; the other one is higher in energy. I'm going to go ahead and label these as sigma and sigma star; the star means antibond. Hopefully, you could go back and figure out that there'd only be one electron in either of the individual orbitals that we use to make up the bond. If you can't figure that out, then remember that a bond is only two electrons, so either both came from one atom, or one came from each; I'm just choosing to show it as one coming from each. There's some justification for that, because in methane, carbon had four valence electrons, hydrogen had one, so take one of each of the valence electrons from carbon, it could make one of each of the sigma bonds that forms. Things roll down hill, so the two electrons go into that bonding orbital. None of them go into the antibonding orbital, which is why we say there's a bond. One of the confusing things about antibonds is: if that antibond is there, how can the molecule exist because if you have an antibond, doesn't that destabilize the system? No, because you always have bonds and antibonds, it's how many electrons are in them, because it's the electrons that are the bond or the antibond. Otherwise, you just have a space called an orbital. So the fact that we actually have electrons in the sigma bond is why the bond is there is why the molecule forms. If we put electrons into the antibond, that's when the bond breaks. To help connect this back, I did mention how the first step [to forming a Grignard reagent] is to put an electron into an antibonding orbital. We can see here that, if all we have is a sigma bond, then that's exactly the only place that electrons can go, in a sigma star orbital.

This is not the full picture, because on top of being able to write an orbital energy diagram, you need to know what does a bond look like. The is probably the most confusing aspect of molecular orbital theory, is that we do the following: we say, alright, there is an sp^3 orbital, which is I'm doing a full orbital diagram I need to draw both the lobes, and there's an s orbital. What if the large lobe of the sp^3 hybrid is the same sign as the s orbital? Two functions that have the same sign add together; let me make this more clear by showing the position of the nuclei involved. We could, instead, imagine a situation where the sp^3 's larger lobe is opposite in sign to the s orbital. We're going to end up with a situation like this: where the point at which the sp^3 and s orbital would overlap each other, they'd cancel each other out, which means there'd be no electrons there, which means that's a node.

Notice that for one case, we end up with electrons between nuclei, which is superscientific notation I'll represent like this [a smiley face]; versus the cancellation where there's no electron density, that I'll represent like that [frowny face]. There's a reason that I use this notation that you'll see momentarily. This is the way that we represent the bond. Does this really happen? No, because those atom orbitals don't exist if you're in a molecule. The whole point of all of this story is to say: here's our model for making a bond. This doesn't look like the hydrogen bond and antibond, because we're using different orbitals; this is to highlight the fact that it doesn't just have to be between two hydrogens to make a sigma bond, it can be any kind of hybrid and any other kind of orbital, as long as they touch head to head, that there's one line between the two nuclei that that bond lies along. That's a sigma bond.

Let's move to a pi bond. In a carbon-carbon pi bond, it's exactly these two interactions that we're looking at, the way of modeling what's going on. Again, we allow these things to overlap, and we end up with shapes that would look something like this, to stylize it. Notice that, again, on the lower case, we end up with electrons between nuclei.

Here we have no electrons between, which is not favorable. If we were to draw an orbital energy diagram, here's what it would look like. We start with two p orbitals, each of which, if it's just a bond, have one electron in it. There's a favorable and unfavorable overlap that's caused because you have two nuclei. The fact that you have these two possibilities comes from the nuclei both interacting with each other and the electron. The lower-energy case is a pi bond and picture-wise corresponds to what we have over on the left, with electrons being between the nuclei, which is why it's lower in energy in the first place. [commentary on explanation for why energy is lower; it's not just because it's lower on the diagram] A bond is lower in energy because electrons end up between nuclei; plus and minus charge come closer together, which releases energy. In the antibond, if you're pushing electrons away from the middle between the two nuclei, then that's unfavorable, that's why it's higher in energy. That's a pi star.

What do we do with a case like this? Because if we drew a SMOG, what would it look like? The following: you have sp²-hybridization on all three of the carbons. Notice that when I'm drawing my sp² hybrids, I do it in such a way where I'm predicting or anticipating that I'm going to be drawing p orbitals in. I try to make sure that my sp²s I don't draw in such a way that they would overlap on top of my ps. Don't forget the hydrogens, which are s orbitals. Since this is a SMOG and I'm not showing sign, I'm going to fill the whole p orbital in. But here's the problem: which of the p orbitals are going to form that double bond that's shown in the diagram? [story about Dad] The answer is yes, because all three of the p orbitals overlap. That's what conjugation is, that's what resonance is, but what do we do to represent that, using atomic orbitals? There's a couple of principles that you've got to learn, which is: the number of molecular orbitals generated in a pi system – that's where multiple p orbitals overlap – is equal to the number of p orbitals used to represent the system.

The point of this is what is a quantized energy system, which is really the point of this wave demonstration. Because this is the way that we're going to represent these different pi systems. Think about the bonding picture that I just had here for a simple pi bond. One way we could go back to view these pi bonds is to say: here's the lowest-energy function, and here's one higher function. Notice that the bottom function never crosses this axis in between the two; it's as if we made the two p orbitals the boundaries within which this wave, this electron can exist. If we go up one level energy, then if you have some kind of system within which the endpoint are fixed, the lowest energy level possible is one in which the functions spans the two points without a node in between. But if you go up one level in energy, then you've got a node there. You notice that the two halves, if we could take a stop-frame of this, one half will be pointed in the opposite direction from the other; but in the middle, there's nothing. Remember that electrons are waves and the waves, the way that we interpret it is that the probability of electron being somewhere; if the way is always zero, you never have an electron there – that's how we end up with an antibond.

But what happens if we end up with a system where there's three nuclei? Then you'd end up with a case where you could have a third energy wave, where there's now two nodes. Notice that those two nodes are symmetrically spaced, where you divide the space evenly into thirds. The whole point of that is to show you that you can use a wave equation to match or represent the p orbital representations – let me draw what I'm trying to say. If you have three p orbitals, you have three molecular orbitals that you generate. To superimpose, here's a function that spans, spans with one node, spans with two nodes. If we make the three nuclei to be evenly spaces, as they would be, then if we were to fill in the shading to match that wave we superimposed, you'd shade them all the same way; that would put electrons between all the nuclei; that would be the lowest energy possible; that's why I wrote it at the bottom here. The opposite case, up at [the] top: notice that you have nodes in between. In fact, this is worst possible case, where between each atom there's a node. If we wanted to fill in the sign of the wavefunction that would give us the same-looking creature, each one's going to be opposite the other. That means that's there going to be no electrons between nuclei; that's the worst possible energy, so that's why it's written up above; it's highest in energy.

What about that middle orbital? You notice that the node passes right through where one of the atoms would be. That means that, in the representation of the wave function, we don't use that orbital. How could that orbital just disappear? They all disappear because it's a bond, so none of those atomic orbitals exist. So don't worry about the poor atomic orbital; worry about how we use it to represent this system. We're going to use the orbitals at one end or the other. There's a sign flip that happens, because there's one node. The phone cord demonstration was to show you the physical example of going from zero to one to two nodes. Energetically, what do we get? We get a bond, where electrons are between all atoms; we get an antibond. But then, we also get a non-bond, which means it's the same energy as if nothing happened in the first place. If you think about it, if this really was a molecular orbital whose general shape could be represented by this overlaid function, and if that function really passes through zero at this point, then it's as if the two other portions of this orbital don't have any interaction with each other at all, that electrons aren't really between anything. It's neither an increase or decrease in energy; that's a non-bond.

– Atomic orbitals (AO) describe the possible locations of electrons in a mononuclear system. All AOs have shapes that depend on only one nucleus and are symmetric about that nucleus.

– Molecules contain bonds which are the interactions of two or more nuclei. Because multiple nuclei are involved, AOs cannot be directly used to explain molecular structure (methane).

– Hybridization involves combining AOs on the same atom to create new molecular orbitals (MOs) that match the geometry of the system (match VSPER).

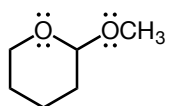
– Bonding can be represented by using AOs on different atoms.

CH4 – Structural Molecular Orbital Graphs – a graphical depiction of the types of orbitals present in a molecule, ignoring sign of the wavefunction.

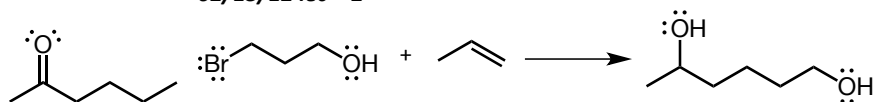
The # of MO generated in a pi-system = # of p orbitals used to represent the system.

Structures

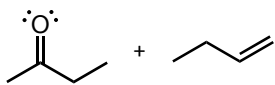
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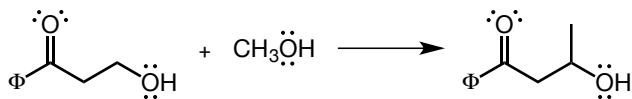
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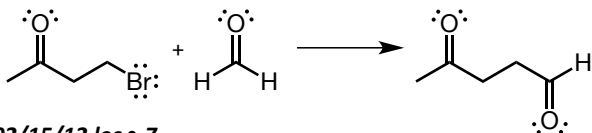
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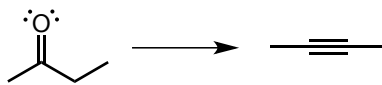
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