

Lecture 12B • 02/14/12

Here is a set of synthesis problems. [homework]

Conjugation

Conjugation is just an extension of the type of molecular orbital theory that we've already covered. I'll start at the beginning. Molecular orbital theory is based off of atomic orbitals. We have a way of using atomic orbitals to represent both the structure of molecules and bonding. We're going to be talking about bonding. Bonding is an interaction between two – or more – atoms. Why does a bond form (there's a good place to start)? Something can be more stable; what does more stable mean? Not octet, because not everything follows the octet rule. Bonding occurs because energy is released. That's the model that we need to redevelop. We talked about two different ways of showing that release of energy. We talked about + and - charges and whether they're attracted to each other or repelled by each other, but if we're talking about little charges, then we're treating them as particles, which is the wrong picture, because subatomic particles really act like waves. We have to have some kind of description of a bond that takes into account the wave behavior of an electron. That's how we end up talking about atomic orbitals, because if you're talking about waves, you're going to be talking about wavefunctions, quantum mechanics, you've got to start with an individual atom, which is a complicated enough story as it is. Unfortunately, we can't use the atomic orbitals directly to describe bonding, so even though you might spend all that effort to understand atomic orbitals, in one sense, you'd have to say that it all needs to be thrown away when we're talking about molecules. Except, there is a way to use atomic orbitals to model what happens in molecules and model what happens in bonds. That's the connection that we need to start with: how do we make the transition from atomic orbitals to molecule orbitals, why is there such a transition.

Is there really such a thing as an atomic orbital if you've got a molecule? No, why not? That's what we do, but why can't you just use atomic orbitals directly? Because there's more than one nucleus present. The unique shapes that atomic orbitals make, if you think about them, the s orbital is completely symmetric around the center, a p orbital is even split in half at the point of the nucleus, a d orbital is a flower shape, again with the nucleus right in the center. All of those unique shapes are created by the fact that you've got just one nucleus. As soon as you put in a second nucleus into the system, then you're going to have attractions between the electron and both of those nuclei, which is automatically going to change the shape of the orbital that you have. That's our first set of thoughts there: that atomic orbitals (AOs) describe the possible location of electrons in a mononuclear system – something that only has one nucleus.

There's a further thought, which is that these equations for atomic orbitals can be exactly solved, as long as there's only one electron around. When I say polynuclear, that doesn't refer to the number of protons; regardless of the number of protons, if you have just one electron, you can actually sit down and work through the integrals to come up with the equations for atom orbitals. When you start having multiple electrons, then there's too many bodies in that problem; you can't come up with enough equations to solve for this system. But, atomic orbitals still exist, we just can't write the nice equations for them. As I said a moment ago, all atomic orbitals have shapes that depend on there being only one nucleus present.

The next part of the problem is what do we do when we get to a bond, because a bond has multiple nuclei, and if you have multiple nuclei, then, at least directly, we can't use the atomic orbitals. As we'll see in the models that we use, sometimes we use atomic orbitals, cause it gives a good enough picture of what's going on. Molecules contain bonds, which are interactions between two – or here's the key part – two or more atoms. Because multiple nuclei are involved, atomic orbitals cannot be directly used to explain molecular structure. [methane] This is the example I always use to show how atomic orbitals won't work in a molecular system. If you recall, for carbon, we have the valence orbitals of carbon, which are s and p orbitals; they're different shapes from each other, and they're also different energies than each other – that's one key thing that happens in polyelectronic systems, that because of the multiple electrons that are there, it ends up causing a difference in the energies of different kinds of orbitals that are all part of the same shell. If you only had one electron, technically s, p, d, f orbitals are the same energy as each other, but they're not, in most atoms. But if you look at methane, methane is a molecule where the bond angles are 109.5° , which doesn't match at all either the s or p orbitals in terms of geometry; and, all of the bonds in methane are equal in energy to each other, but the different orbitals in carbon are different energies from each other.

What we do is this thing called hybridization, where we blend the different atomic orbitals; we don't throw away all that work to understand atomic orbitals, we just use it by creating a model, where we add and subtract the different ones, the different atomic orbitals on the same atom to come up with hybrids that are going to match the real-life geometry of that system. Hybridization involves combining atomic orbitals – here's the key part – on the same atom to create new molecular orbitals that match the geometry of the molecule, to match the predictions of VSEPR theory. VSEPR theory's a very simplified theory that gives us a good prediction of what the different shapes of the molecule's going to be; it's just based off of repulsion, that like charged objects are trying to get as far away from each other as possible. Of course, once you do that, we end up with a geometry that doesn't match all the atomic orbitals. Because of the crazy symmetry that's in atomic orbitals, we can combine them and magically, somehow, get these different hybrids that happen to have just the right shapes.

That still doesn't get us to bonding, per se, that just helps create an orbital set to help explain the structure. But then bonding, what we do is the same type of thing, except that instead of adding and subtracting orbitals on the same atom, we're gonna add and subtract orbitals on different atoms; that's the difference. Bonding can be represented by combining atomic orbitals on different atoms.

To show an example of this, I want to start with a sigma bond. Instead of starting with a plain hydrogen-hydrogen sigma bond, I want to take a slightly more complicated situation, which is the sigma bond that we would have in the molecule methane. [SMOGs] The SMOG essentially shows you the different types of orbitals on a molecule, but doesn't look at all at the sign of the wavefunction. If an electron is a wave, there's a function that must be able to describe it; that's all a wavefunction is. A wavefunction can also be called an orbital, because a wavefunction describes the space that is an orbital. Wavefunction can have plus and minus values; if you think of p orbital, you shade one half one way and shade one half the other. That's because, mathematically, we look at the equation, one half is a negative sign and one half is a positive. It has nothing to do with charge; electrons are always negative. It has to do with the function. That kind of information you don't put in a SMOG. A SMOG is a graphical depiction of the types of orbitals present in a molecule, ignoring wavefunction sign.

If we had an sp^3 hybrid, and we did use shading, then it would look something like this. Where you have the two different types of shading, switching from one to the other, that means you're flipping the sign of the equation, and that's what a node is – a node is a point where the equation's equal to zero. All hybrids have this node. If you take an s orbital and put it on top of a p orbital, you're supposed to be adding these two things together, the s orbital's going to add to one half of the p orbital because it will be the same mathematical since, but it'll shrink the other half because it'll be opposite sign. That's how we end up with this lopsided diagram. Instead of trying to put all of the little tails in there, which makes the diagram more complicated to read and draw, I made the decision to simplify, where I'll just [draw] one of the lobes of that orbital. It's not that it disappears, it's that I'm being lazy – but I'm also trying to be clear.

What would a SMOG look like for a simple molecule like methane? You draw a picture of all the different types of orbitals that are present, which there are only two: there's an sp^3 orbital, which is what have between carbon and hydrogen. If I say sp^3 , that automatically means there's four of them. Then, of course, there are the four hydrogens. [coloring system] This is a fake diagram, because these orbitals don't even exist, because if you have bonds, a bond is an interaction between more than one atom, how can you have separate orbitals on separate atoms that are somehow sharing the electrons? They don't, but we do this kind of drawing so that we can understand the structure. At the same time, then, we have to recognize there is a bond there, and it really needs a bonding orbital to describe it. What we're going to do now is a molecular orbital energy diagram, which is different from a SMOG, where you write the atomic orbitals that are going to go into making that bond on the side of the diagram, and then you write the new orbitals that are formed, the bond and the antibond, in the middle of the diagram. I'm going to put sp^3 on the left arbitrarily and s on the right, but it's not arbitrary that I've written the sp^3 above the s. Notice that I've already labeled my y axis as energy, so I'm explicitly stating that the sp^3 orbital's higher in energy than s, which we can easily make that statement if we were on the same atom. [is s on hydrogen lower than sp^3 on a carbon?]

If we ignored the difference between the different types of atoms involved, why could you say it makes sense that the sp^3 orbital is higher in energy than s? It's a combination of s and p orbitals; why does the fact that there's some portion of a p orbital in there matter? There's some p character in that sp^3 orbital; why does that cause it to be higher in energy? Effectively, because of shielding, electrons that are in a p orbital are, on average, held further away from the nucleus, which makes them higher in energy. So the more like a p orbital, the higher in energy it's going to be, which is exactly the argument we made to explain why an alkyne is more acidic than an alkene is more acidic than an alkane. Because an sp orbital that's 50% s is going to better tolerate – which means be lower in energy – with an anion than if you have one third of an s orbital – which would be sp^2 – or one quarter of an s orbital – which is sp^3 .

Even though they're different in energy, they're close enough that they can interact with each other. We do form two different things: a bond, which is a sigma bond; and then an antibond, we often use a star to show something is an antibond. The fact that we end up with two orbitals is because we have two nuclei involved. The number of molecular orbitals generated in one of these kinds of bonding systems is, because of symmetry, always equal to the number of atoms that are involved. We had two atoms making the bond, so we end up with two bonding orbitals. How do we fill this up? If you think about methane's case, that's a relatively straightforward one to analyze, because you've got carbon that's got four valence electrons. Each hydrogen has one valence electron; you can imagine, therefore, that one electron each come from carbon to be in that sp^3 hybrid, versus one electron each in the s orbitals. Things roll downhill, so by creating these new bonding orbitals, we're going to end up with two electrons in the bond, none in the antibond.

One thing about this that confuses people often is: wait, if you've got an antibonding orbital, how can that orbital exist, cause doesn't an antibond cancel out a bond. Yes, but it's more correct to say an antibonding electron cancels out a bonding electron. In other words, the electrons themselves are the bond, are the antibond; these orbitals are just space, and space itself does nothing. Once you put an electron in it, that's when the effect happens. The fact that we have electrons in the bonding orbital and not in the antibonding orbital means we really do have a bond.

If you think back to the sodium reduction of an alkyne or the initiation of [the formation of a] Grignard reagent, both of those involve putting an electron into a bond that already existed. If you see this diagram, this shows the empty place where an electron like that can go; it would go into the antibond. [What happens to O²⁻, how does it react further?] This is where these diagrams come into play – examining what kinds of bonds do we have, how many electrons are there, do we therefore have anything in an antibond? That's part of the picture.

Another part of the picture is: what do these orbitals look like? That's where we use the atomic orbitals again. We used them already here to make the energy diagram, but then we use them geometrically to show the shapes of the orbitals, the bonds that form. If we had an sp³ orbital, it's going to have one lobe that's larger than the other. I am going to be drawing these with sign, because if we're talking about bonding, we're talking about adding and subtracting orbitals, we're talking about adding and subtracting equations, so we have to know where it's plus, we have to know where it's minus. We have it interacting with an s orbital. It is unknown an arbitrary which sign of the wavefunction that we use. Remember, these orbitals don't exist in the first place, so it's not that the orbital is somehow interacting in one way and interacting the other. What I'm about to do is put a plus sign in between these and say let's add these together. That's not what happens in real life; that's our model we use. When I say that I'm going to add these things together, I really mean, both geometrically and equation-wise, put one on top of the other. Of course, if they match in terms of sign, that's something we call constructive interference, which means the two functions reinforce each other, and we end up with a fatter orbital. To really show what's going on here, I'm going to put a green line, in this case not to represent the node, but just to show you where the center of each atom is, because you could then see that, in this bottom example, we end up with this new orbital where we have electrons between the two nuclei, which in complicated symbology I write this way [smiley face]. This is related to the question: why does a bond form, or why is a bond lower in energy? [rant about explaining why a bond is lower in energy]

Why is it lower in energy? The answer is: favorable electrostatic interaction – you're putting a negative charge in between two positive charges. That reduces how much each positive charge interacts with each other and increases how much opposite charges interact with each other, which is a favorable thing – that's why a bond happens, because it puts electrons in favorable places. What's an antibond then? Where you do the opposite, where you make it less favorable. If I added these top two orbitals together, then what you're going to find, in fact, what used to be the larger lobe will now be the smaller one; the s orbital will kinda get distorted and pushed out away from the nucleus. What I'm trying to show here is that there's lack of electrons between nuclei, which again in complicated symbology I could write like this [frowny face]. Because if you're pushing electrons away from the space between the two nuclei, the positive charges are now exposed to each other. We're about to see systems in which there's not just two orbitals interacting; we're going to have conjugation, where we have multiple orbitals, so you have multiple favorable or unfavorable interactions; you have to sort out which is greater: the number of favorable interactions or the unfavorable ones. We're going to use that to decide when is something a bond versus an antibond. The fact that you have no electrons between the two atoms means that the positive charges are both more exposed, but yet you're trying to keep the atoms at a fixed distance. That's the part of the picture that sometimes gets lost in the explanation is – you could say the atoms should push away from each other, but we're saying that if you had two nuclei in a position and here's that orbital, what kind of energy do you have? It's high energy because you've exposed the nuclei – bad electrostatics, that's why an antibond is higher in energy. Anywhere you have complete cancellation, that's a node, which means the value of the function is zero, and since, in the Borne interpretation of quantum mechanics, it's the square of the wavefunction that's related to the probability of finding an electron somewhere. If you have a node where the function is zero, that means no electron exists there. Why is this a sigma bond? Because the orbitals are all aligned in the same line as each other. Any time orbitals overlap like that – not just two s orbitals, any two orbitals – overlap [directly] like that, that's sigma bond. What we should do next is a pi bond.

[phone cord demonstration] The real purpose of this is to show quantized systems, quantized energy. There's only one specific type of function that's going to be able to bridge between these two fixed endpoints – a function that starts at one endpoint and ends at the other. There's various function that can fit that set of boundary conditions, one in which you have just a smooth function that spans between the two points, or, if you were to add enough energy, then you get a function that has a place in the middle where it appears that it's not moving; that's our node. If you were able to take a stop-motion picture of this, you would see that the two halves of this wave are pointed always in opposite directions from each other. You go up one more point in energy, you get a function that is split twice; where one part is pointing is opposite the middle is opposite the other end. The point of this demonstration is to show there is no one-and-a-half wave, or two-and-a-quarter wave; it's either one or two or three different segments that you get. The only way the wave can exist is, again, if the start and the end are at these endpoints. Think of it this way: if an electron is a wave, think of a line of p orbitals being like a box that you put that wave in. It turns out that the equation for the wave must fit within that box, means it must end at the two ends of the box. If you have two p orbitals, one possible wave that could exist across those two p orbitals is for it to just simply connect across, which is you did that and this is a wavefunction, and the maximum value of that wavefunction's right in the middle between the two nuclei, that's what we call a bond; this is the lowest possible energy you could have for that system. You go up one rung in energy, then what happens? You put a node right between the two ends, which, if you're talking about a pi bond, one atom's here, one atom's there, there's a node in between, that's the antibond.

Where we're going with this is what happens in you have three p orbitals. You could have one wave that spans across like this, that's one energy level; another energy level would have a node in between, and another energy level where there's two nodes in between. Let's see how we model that on one of these bonding diagrams. [need for math to explain quantum] We have a pi bond; how can we represent that? Two different ways, the two different types of bonds that form. We represent it by using two different p orbitals. In real life, there's some kind of orbital that forms; this is just a way of modeling it. To relate this to the phone cord demonstration, another way to model it is to say the lowest energy standing wave possible is one that bridges between the two endpoints. The next lowest energy wave possible is a wave that has one node in between. If we were to add two p orbitals with the same sign of the wavefunction, that's what we're going to generate – a shape in which the sign is the same all the way across. If, instead, we added two p orbitals with opposite sign, then we're going to generate an orbital with a shape that looks like this: it has a node between the nuclei. So here we have electrons between nuclei, again favorable; here we have no electrons, which is unfavorable. Where you have electrons between, that drops the energy so we call that a pi bond; where you do have cancellation so it's higher energy, you end up with an antibond. You have a system that already has a node through the atoms, but we don't look at that, because that's already part of the system. The fact that you start out with a p orbital means that it's higher energy than an s orbital, but then when bonding and antibonding happen, since you already have that node through the two nuclei, it doesn't influence whether or not it's a bond or an antibond. It matter what happens between the two nuclei.

What happens if we have the allyl case? First, let's do a SMOG for that. Each of the carbons there would be sp²-hybridized. When we say sp² hybrid, that automatically means we have three hybrid orbitals. From experience, I know that I'm going to be writing a p orbital superimposed on top of all of these, so I'm going to draw my sp²s carefully enough that I don't interfere with my ability to draw the p orbitals later on. We do, of course, have a flock of hydrogens. Then, we have p orbitals. Which of the p orbitals overlap? All of them, or yes. And no. [story of Dad] If I asked, is it the left two or the right two orbitals that overlap, the answer is yes; they completely overlap, which is the whole point of what resonance is and conjugation is. Resonance is the fact that we can't write one structure for the molecule because the bond doesn't exist just between two atoms, and we don't have a writing system that handles bonds that span multiple atoms. This also has an effect, therefore, on how many energy levels there are, because when we had just two orbitals involved in bonding, it made two new molecular orbitals. Because of symmetry, when we have three atomic orbitals that go in, we're going to have three molecular orbitals that come back out. We're going to have the p orbitals be used to represent those three molecular orbitals. The question is: how do we properly use the p orbitals to show what the real molecular orbitals look like?

Let's superimpose on top of it the same type of wave pattern that you saw earlier with the phone cord. It might make sense that the lowest energy orbital that's possible is that all the p orbitals have the same sign of the wavefunction, which would match a wave that spans only in the plus or minus direction across the system. If we go to the top system, you notice that the wave that I have there, there are two nodes in it. If I'm keeping track of the number of nodes, we have zero and two. Number of nodes matter because that's related to the principle energy level. That's what the in the n, l, m_l, m_s is – really, it's the total number of nodes [plus one]. But if we did have a node between each atom, that means that we have cancellation between each atom. Down here, I could show that I've got two favorable interactions; that means that this is going to end up being a bond; up top, I can show that I've got two unfavorable interactions; that means I have an antibond. What about the middle picture? Because, this wave way of representing the orbital, I have a node that passes right in the middle; it passes right through where one of the atoms is. What does that mean? We don't use that atomic orbital in representing the molecular orbital. How can an orbital disappear? None of them exist in the first place, so don't worry about it disappearing; it's not there. It's just that we don't use it to represent the molecular orbital; the node passes right through it. If so, we could write one shading on one atom on one side, the opposite shading on the other atom on the opposite side. They're too far apart from each other, that they don't interact. It's neither favorable nor unfavorable; it's what we therefore call a non-bond – energetically zero relative to the original atoms. [extension to larger linear systems and benzene]

Conjugation

- Atomic orbitals (AO) describe the possible locations of electrons in a mononuclear system. All AOs have shapes that depend on only one nucleus being present and are symmetric about that nucleus.
- Molecules contain bonds which are the interactions of two or more atoms. 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 – Identical to those from lecture 11A (02/13/12)