

## Lecture 3B • 09/30/11

### Bonding

The reason we're reviewing this is to get an idea of the type of bonding in organic molecules, which does involve both sigma and pi bonds, so we need to review what's the difference between the two of those. I'm also going to be talking about what a bond versus and antibond is.

Let's start first with a classical picture of bonding. The whole reason a bond forms is that energy is released. A way of thinking about it is: if you have one nucleus here, one nucleus here, those are both positively charged; if you have electrons between them, then that acts as the glue to bring those two nuclei together. Otherwise, if you had plus charge that was interacting with plus charge, that would be something that's unfavorable electrostatically. One of the few things we need to know from physics is: like charges repel, opposite charges attract. Let's draw a picture, where we have a nucleus, and another nucleus, and let's say that this is a hydrogen molecule, and we'll have, therefore, two electrons. To keep this the simplest possible example, let's say this is protium, so hydrogen that only has a proton and no neutron, and then one electron for each hydrogen.

There's different kinds of electrostatic interactions that are going on here. There is the interaction that could occur between nuclei, depending on how close the nuclei get to each other. In a very technical way, I'll just represent it like this. Same thing for electrons: if you had electrons that are interacting with electrons, that's also not a favorable interaction. What we're wanting, then, is electrons interacting with protons, which even more ideally we want an interaction from one nucleus with the opposite atom's electrons, bringing these two atoms together. We can draw a diagram, an energy diagram. For this diagram, we're going to arbitrarily assign a value of zero for when the two atoms are infinitely far away from each other. We just assign that as a comparative purpose. As those atoms get closer and closer together, then we're going to see what happens energetically. If we're saying that, infinitely apart from each other, there's no interaction, then that's why it's zero. As you start to let the atoms approach, then these favorable interactions between electrons and nuclei outweigh the unfavorable interactions with either electrons with themselves or protons with themselves. So the energy is going to drop if first.

Then, if you were to continue pushing the nuclei closer and closer together, at some point, those nuclei start to bump into each other; then, the energy of the system will start to rise again. If you kept on trying to push them closer and closer and closer together, then the energy is just going to keep going up, at some point, exponentially, because you're trying to squash the two nuclei on top of each other. So the energy curve would look like this. Dropping down to some minimum point; as you start pushing these things closer together, energy goes up again. This  $r$  would be the interatomic distance.

The whole reason that bonds form is that energy is released. This quantity of energy that you would have to add in to raise this system back apart again, to break the bond, that is bond dissociation energy. If you took the distance from zero to this optimal point where you have the lowest energy, then that is the average bond length. For the most part, this bonding picture does a reasonable job at predicting what a bond between two hydrogens (not a hydrogen bond) would look like. But if you did the same thing for helium, this model doesn't work anymore. Helium does not form a molecule with itself. One way to rationalize that is to say, "Helium is not a noble gas." And noble gasses, since they have octet configurations, or for helium it's a duet configuration, those don't normally react. But that's not really the full story of what's going on. If we force them to react somehow, it still turns out that what molecule results would still not be isolatable, would not be stable.

Could anyone tell me why this particular model is inadequate for helium? We know there are these things, bonds and antibonds. What is it about the wave that I set this diagram up that fails to account for antibonds? Where do antibonds come from? Phase, that's something related to a wave. Do you see something related to a wave representation anywhere in this diagram? That's the point: electrons are not just particles. I just wrote little points here, totally ignoring the wave characteristics of an electron. That's why this model fails: this is a classical model, a non-quantum model, in which we're treating the charges just as points. These are not just points, and that's why this model does not work. Why go through this model, then? It is a convenient way to introduce this idea of bond dissociation energy and bond length. For some systems, like the hydrogen molecule, it does work. This classical model can be used to describe the hydrogen diatomic molecule, but fails to describe helium. This is because the electrons are treated as particles, ignoring their wave-like behavior.

In order to talk about the quantum model, we need to talk more about waves. First, a little bit about the anatomy of waves. A simple sine wave I've written. Don't worry about what the y-axis is, just assume it's some sort of sine function. If you did measure the distance between the x-axis and the top of the wave, what is that quantity called? The amplitude, how loud the wave is. The distance between the origin and the first complete repetition of this wave, what would that be called? There's a couple of different terms, depending on what that axis is. If it is time, then this would be period, how long does it take for a wave to complete. If it was distance, then it would be wavelength, how long is the wave. Let's presume for the moment that this is a distance scale, so we'll call this  $\lambda$  for wavelength. Frequency, we can't really show, in a sense, since we need both time and distance to establish that. There's one more thing that could be shown on this axis. In order to do that, I need to draw up two waves that are slightly offset from each other. Although these many not be perfectly drawn, what I'm trying to show is

that these are two otherwise identical waves, but one that starts right at the origin and one that does start a bit later. That distance between the two, what is that called? The phase of the wave, which is sometimes represented by the letter phi.

The reason I need to show you this is in the context of a discussion of constructive and destructive interference. I want to describe situations of perfect constructive or destructive interference. First, imagine this situation, where you have two different waves, and let's say they're two completely identical waves: same frequency, same wavelength, same amplitude, and same phase. If you were to superimpose these two functions on top of each other, just simply add the functions, at every point along both of these curves you have exactly the same value. If you had an arbitrary amplitude of one, then this would be  $1 + 1 = 2$ . Again, at every point the value of one wave [perfectly] reinforces the other. This is an example of perfect constructive interference.

Now let's look at perfect destructive interference, which would be when you have two waves that have the same amplitude and frequency, but with exactly opposite phase. Because each of these exactly matches each other, but in the opposite sense, then everywhere along the curve they're going to cancel each other out, which means you'll end up with nothing. This is perfect destructive interference. Which is how noise cancellation headphones work. If you have a noise cancellation headphone, you've also got a microphone in the headphone that is listening to outside ambient noise. When that noise hits your ear, at the same time, the processor in the headphones is sending the same signal as the noise from the outside, but turned the opposite phase. By the time the music that you're listening to, the ambient noise you're listening to from the outside and this third signal, that's the inverse of the ambient noise, hits your ear, the signal being generated by the headphones cancels the ambient noise from the outside, so all you hear is the music. So that's noise cancellation – destructive interference.

Where does this come up in bonding? Let me show you the end result. Just as the presence of one nucleus establishes the shape of all these atomic orbitals, if you've got two nuclei forming a bond, the two nuclei now form a new set of boundary conditions, which generates a new set of orbitals.

The end result is the following: in the hydrogen molecule, we have two possibilities that occur. The black dots will represent the nuclei, and orbitals will go around these nuclei. One of them, the orbitals, will look like this, where you have electron density that's spread all throughout the molecule. The important point is, there's electron density between the nuclei. We have a negative charge between two negative charges, that's the glue that can bring these two things together. The more plus and minus that interact, the more energy that's released and the stronger the bond's going to be. What does the other orbital look like? Notice I've got one orbital drawn above the other; to make this more explicit, let's say this is increasing energy. Just like in the phone cord system, when I went from one energy level to the next, what occurred? What did we see physically, what appeared? A node. A node will appear in the molecular orbital in this bonding system when you go up one more energy level. Here is the node, so this orbital is divided into two. Notice that means we have a lack of electron density between nuclei.

The lower orbital, where you have electron density between the nuclei, that's going to be lower in energy than if this bond had never formed in the first place. In comparison, the other molecular orbital that's formed, because you have a lack of electron density between those two nuclei, the two nuclei are exposed to each other, which means that orbital is higher in energy than if nothing had happened in the first place. That's why this the lower one because it releases energy, we call a bond, and that's why this other orbital that forms, because it's higher in energy, we call an antibond. This orbital is an antibond because its energy is high than the energy of the two atoms if they had not interacted. This orbital is a bond because the energy is lower than the isolated atoms. Mathematically, wouldn't it be nice if we had some way of modeling these orbitals? Turns out there is: we can use the atomic orbitals.

The shapes of atomic orbitals are generated by having only one nucleus. We have more than one nucleus now which means technically you can't have atomic orbitals any more. The math behind these atomic orbitals is incredibly complex. After spending all that time getting an understanding of atomic orbitals, if we could use them model molecular orbitals that'd be nice. What we do is the following: we use what is called LCAO – linear combination of atomic orbitals, which means atomic orbitals are added and subtracted in such a way as the estimate molecular orbitals (MOs) such as bonds and antibonds. How would it work in this case? They hydrogens each have an s orbital. Let's take that s orbital function. If we were to take two different s-orbitals that had the same sign as each other – remember that these orbitals are represented by wavefunctions, and wavefunctions are just functions, so they can have positive and negative values. If you took two different s-orbitals that had the same sign and you put them on top of each other, there's only going to be constructive interference; the functions are just going to reinforce each other. That's how we get something that looks like the bonding orbital.

If we took the same two [s]-orbitals and we allowed them to be opposite of phase of each other, then it's like adding 1 and -1 together. But remember that this is not a system where the nuclei are going to be exactly on top of each other, so you're not going to have complete destructive interference. As much as they do overlap, that destructive interference is going to occur, which is how we end up with the orbital that looks like this. You might ask: how do these orbitals know that they're opposite sign? How do you know if they're the same or the opposite? You don't, because this doesn't happen. Because there aren't any atomic orbitals, because it's a molecule. This is just a model that we use to try to understand these molecular

orbitals, so don't waste any time trying to think, "Wait, how do you know what it's going to be?" We, as humans, make it both on paper. We create these molecular orbitals by adding together atomic orbitals.

This is a specific type of bond where, if I was to draw a line through these nuclei and spin these orbitals around, the orbitals don't change their shape or sign when rotating along that interatomic axis. This is a sigma bond. To show an antibond, we often use a star.

Phase doesn't have physical meaning; the square of the function has physical meaning.

This is how we can predict what happens in the helium molecule. This is the part where the classical model fails, because it doesn't get into any of this wave business. How do we make a model for helium? What we do as a diagram is the following: we establish our zero energy which, by convention, would be the non-interacting atoms, kinda like the classical model where we assumed that zero meant nothing's going on. In the case of hydrogen or helium it would be the 1s orbitals that interact, so on the outsides of this diagram we show these atomic orbitals involved. On the inside of the diagram, we show the different molecular orbitals created. In this case we have the sigma and the sigma star orbitals, the sigma bond and the sigma antibond. These filling rules apply to molecular orbitals as well as atomic orbitals. If we have the case of just hydrogen, there's only one electron to start with on each s-orbital. When those orbitals disappear in making the bond, the electrons have to go to whatever new orbitals we have available. The lowest-energy orbital is now a sigma bond, so Aufbau principle: the sigma bond fills up first. Pauli exclusion principle, you can squeeze two electrons in that orbital, as long as they're opposite sign, so the two electrons will just go into a bonding orbital. So we know that hydrogen forms a bond.

How is this different in helium? Same diagram, because the same orbitals are involved. But this time, you'll have two electrons per atomic orbital that we started out with. Again, those atomic orbitals will disappear when we make molecules, the electrons have to go somewhere, and only two of the electrons end up in that bonding orbital, which means the other two get pushed up in energy; they must go into the antibonding orbital. Hydrogen forms a bond because only bonding orbitals are filled. Helium fails to form a bond because for every bit of stabilization that you get by an electron falling into a bonding orbital is erased by the destabilization that you get when an electron is pushed up into an antibonding orbital. In general, we have this thing called bond order, which is the number of bonding electrons minus the number of antibonding electrons, that whole thing divided by two. Essentially, each antibonding electron cancels out the benefit of each bonding electron. Each antibond electron causes a destabilization, an increase in energy, that negates the stabilization, the decrease in energy, provided by a bonding electron.

A bond is always, always, always a situation where energy is released. {Parenthetical note about bio texts and bond energy}

There are different ways to model these systems. We could go through a much more extensive discussion of diatomic molecules, but I completely want to avoid that because where we are headed is hybridized molecules, to hybridization. But, we need to do the two-atom system before the multiatom system. My presentation of pi bonds is going to be simplified.

Let's look at the pi bonds. The example system that I'm using is diatomic oxygen. The approach we're going to use is to assume that, before those oxygens approach each other, we still have the atomic orbitals on each oxygen. So just like we used the atomic orbitals on each hydrogen to estimate the bonds, we'll use the different orbitals on oxygen to estimate the bonds. What kind of orbitals are available in the valence shell of oxygen? We have p-orbitals, but any time you have p-orbitals, you have s-orbitals. You might say that oxygen's configuration is  $1s^2 2s^2 2p^4$ , but, all of those p-orbitals would potentially be there, even if they're not totally filled. We could say here's one oxygen; here's its s-orbitals and the three different p-orbitals that can interact. Here's another oxygen, and here's another set of p-orbitals can interact. We imagine that all of these interactions happen at the same time.

There will be two different interactions between p-orbitals. There'll be one set of p-orbitals that directly overlaps with itself head-to-head. To anticipate, this is going to be a sigma bond. Even though it's made of p-orbitals, the p-orbitals are collinear, so draw an axis through them, they would be rotationally symmetric. Then we have these other p-orbitals, two sets of them, that won't directly overlap. There's a sideways overlap that can occur. Let me take those orbitals out, isolate them, and do the same thing we did describing a sigma bond.

If we had two p-orbitals that are going to interact with each other, there are again two opposite situations possible; one in which the phase of both halves lines up with each other; and one in which the phase of each orbital does not line up. If we were to combine these, then we're going to form two new types of molecular orbitals: one that has this very odd shape to it, but one in which there's still electron density flowing across the system, and there is no node between atoms. There is, because we're using p-orbitals, a node that passes through the atoms. That's ok, because we still have electrons between atoms, so this holds together as bond. What would the other situation look like? Since we had destructive interference, not only would we have the node through the atoms, but we'd have a node between the atoms as well. You can see that electron density is therefore pushed to the outside of this system. One way of looking at it is that, since the electrons are on the outside, really the electrons should be pulling the nuclei apart, so it therefore takes energy to hold the system together. Another way of looking at it is that

that two positive charges are exposed to each other, so to keep them at this distance requires some energy. The bottom system is a pi bond; the top system is a pi antibond, or pi star orbital.

In diatomic oxygen, we have four kinds of orbital interactions: s orbital with s orbital; the p orbitals that are directly pointed at each other; and then the two sets of p orbitals that are parallel to each other. The s orbitals will form a bond and an anti bond. One set of p orbitals also forms a sigma bond and anti bond, and then the other sets of p orbitals form pi bonds and pi antibonds. Oxygen has a total of six valence electrons, so between two oxygens we're going to have twelve electrons that we have to throw into orbitals. Starting at the bottom, two electrons go there. Next energy orbital, two electrons go there. Next energy, two. Next energy, here's our first application of Hund's rule: if I only put in two more electrons, one electron each would go into one of those pi orbitals, then throw two more electrons in, one electron each would pair up. We've now used ten electrons up, we need two more to throw into here. This would be our picture for oxygen. For bond order calculation, we would find a total of eight bonding electrons and four antibonding electrons. So  $(8 - 4) / 2$  gives us a double bond, which is what we do observe for oxygen.

Any time you have p orbitals involved, you're going to have orbitals as well. For all the molecules we're going to see in o-chem, any time there's pi bond, there's going to be a sigma bond underneath it. But not always because there's going to be p orbitals.

### Hybridization

We used atomic orbitals successfully to model diatomic systems. But here's the big problem. The molecule methane, CH<sub>4</sub>, has a tetrahedral structure. What is the approximate bond angle between any two of the carbon-hydrogen bonds? 109.5°. Carbon is in the same row as oxygen, so carbon has the same atomic orbitals available as oxygen. Let's draw a picture of that. In polyelectronic systems, when you start putting extra electrons, it causes shielding and penetration effects. It causes the energies of s and p orbitals to be different from each other. If you had a single electron in a atom, regardless of which orbital it happens to be, all of the s, p, d orbitals within a shell would have the same energy. In real life, for carbon, the s and p orbitals have different energies than each other. That means there's two problems here: how do we get from atomic orbitals with 90° angles to a molecule that's got 109.5°? You can't use the atomic orbitals directly; it just doesn't match. Then there's a second problem: the s and p orbitals in a polyelectronic system are different energies than each other, but if this is a perfect tetrahedron, then each of these bonds has to have exactly the same energy?

So what's going on here? It's the fact that you don't have atomic orbitals, since it's a molecule. In order to describe it, then, we have to come up with some kind of system, and that's what hybridization is. Just like we added and subtracted atomic orbitals on different atoms to make up bonds, we're going to add and subtract orbitals on the same atom to come up with a new set of orbitals that just happens to have the right geometry and energy to match what we see in real life. The atomic orbitals of carbon cannot be used directly to describe the molecule methane since the geometry of the orbitals does not match and the energy of the orbitals is not the same. To describe methane, a set of hybrid orbitals are created by adding and subtracting orbitals on the same atom.

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quantum bonding model  
sigma & pi bonds

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