

Lecture 3A • 09/30/11

How many of you have read the sections assigned for the first two days of class?

We're going to start with a classical version of bonding, and we're going to use the hydrogen molecule as the example. Let's make it the simplest hydrogen molecule where we only have protium involved. So we'll have one proton and one electron, another proton and another electron, that are interacting. So we could draw a little diagram like this. Here are our protons, here are our electrons. There's two types of electrostatic (charge) interactions that we could have. There's some unfavorable ones – for example, if the two nuclei were to get too close to each other and start interacting. It's one of the few things for physics that we need to know for this course that like charges repel, opposite charges attract. So, to notate that, I'll use this ever so sophisticated symbology. The same thing would happen if we had the two electrons interacting with each other. They would also not interact favorably. We then, of course, have if one electron interacts with a proton, with a nucleus. That is going to be a favorable interaction. And even better would be if we had one proton interacting with the opposite electron.

What we can do is construct a diagram, where we imagine these two atoms start infinitely apart from each other. We'll assume a relative energy of zero for that case. No interaction, no relative energy. Then we can see what happens when those two atoms slowly approach each other. It's going to look something like this. Infinitely away, we're gonna assume no interaction, so zero energy. As we let those atoms start to approach each other, the favorable interactions occur first. The electrons will interact with the nuclei, and that causes the energy to drop. This is the one and only reason a bond would form, because bonds are always the situation where you lose energy when you form them. You might see in biology texts regarding ATP something along the lines of "energy is released when this bond is broken". You've got to be very carefully reading something like that, because you never release energy breaking a bond, you always have to add energy to break a bond. In that situation that I described, what's really going on is there's a multiple step reaction, where yes somewhere along the way a bond is broken, but the energy release that occurs happens somewhere else in the cycle. Whenever you form a bond, that releases energy. As the atoms start to approach each other, the energy drops, drops, and then at some point, you reach the lowest energy. If you continue to squeeze the atoms further and further together, closer and closer together, then the electrons start bumping into each other, the nuclei eventually start bumping into each other. In fact, if you get them real close, that energy starts shooting way up really quickly. Again, using complex symbology, this part of the graph represents where those favorable interactions outweigh the unfavorable, and here where we have above-zero energy, that's because that's where the repulsions are more prominent than the attractions.

There's a couple of other things we could notate on this diagram. A bond is always a situations where you're releasing energy. If you compare the zero energy, where they're infinitely apart, to this lowest-possible energy, that's called bond dissociation energy. If we look at the distance between having the atoms complete stacked on top of each other, versus this optimal position, where you've reached this lowest energy, that's going to correspond to the average bond length.

And so this is a useful model just to talk about bond length, bond dissociation energy, and the fact that it is an energy drop that causes the bond to form. But, although this diagram is good for hydrogen, it does not describe helium. Helium, when you take two of them and put it together, will not form a molecule. What you could say is, "Of course it won't, cause they're noble gasses. Things that already have an octet (or since this is helium a duet), they don't want to react." But that's not the most complete way of putting it. There's gotta be something going on here that the diagram's missing, that that's why it fails to describe helium. What's the drawback of this diagram? What are we totally overlooking? Because electrons behave like waves. In these diagrams, you can see the way I've written it, we're treating these things as particles. Yes, an electron does act pretty much like a particle, but it acts very much like a wave as well. This classical description, where we're treating these electrons as particle, is inadequate. It fails to describe the case like helium. This classical model of bonding is able to describe hydrogen (the diatomic molecule H₂) but it fails to describe He₂ because it treats electrons as particles and does not take into account their wave behavior.

Before we can cover the quantum model, we need to go back and talk about waves again. We are going to be talking about constructive and destructive interference, which is something that waves can do. So let's learn a little about the anatomy of a wave. For simplicity's sake, let's say that we have some arbitrary y-axis and that the x-axis represents distance. I'll put up a simple sine wave. There's some features of this wave we can identify. If wanted to talk about the distance along the y-axis from the center of the wave to its highest, or lowest, point, that quantity is called amplitude. How loud is the wave, you could say. If we're talking about the x-axis as being an axis of distance, if I talk about the distance from the beginning of a wave to its first repetition, what is that going to be called? The wavelength, which we often represent with lambda. If this was a diagram that had the x-axis as time instead, then we could call that what, that distance? Frequency is how often something happens. The period, that's how long it takes for the repetition. There is one more thing that I can represent on this digram if I draw two waves in comparison to each other. I'm trying to draw two identical waves, except for the fact that they have different starting points, one on the [x]-axis, and one a little bit off of that axis. What is the quantity that represents that separation called? Phase, which that's often indicated by the letter phi. Frequency we can't really show on here because we need both distance and time simultaneously, but there is a relationship between wavelength and frequency.

What are constructive and destructive interference? Let me show you perfect examples of each of those. Imagine, for example, that we have two waves, two waves that are identical in every way. They have the same amplitude, same wavelength, and the same phase. These waves are just functions, and if we imagine that the waves had an amplitude of one, then this is a case of $1 + 1 = 2$. Because at every point along those waves, they're going to exactly match each other, so they're going to exactly reinforce each other, and you'll end up with a wave of amplitude 2. Because there's this reinforcement, since they have the same sign at every place, that's why this is called constructive interference. What about the perfect opposite example? What if you have two waves that had the same amplitude and wavelength – so in a way they're identical – but what if they're exactly opposite in phase? So now we have the same amplitude, wavelength, and opposite phase. This would be like adding one to negative one, because at every point along the wave, one wave is doing exactly the opposite of the other, so you'll end up with flatline, you'll end up with zero, with nothing. This is the perfect case of destructive interference. If you had two waves that weren't exactly the same as each other, then you might have a combination of constructive and destructive interference. So constructive is whenever the signs are the same and the function increases, and destructive is whenever the signs are opposite and you have a disappearance of the function.

As an aside, destructive interference is the way that noise-canceling headphones work. On a noise-cancellation headphone what you've got is not just a headphone but a microphone. That microphone is listening to the outside ambient noise. As that ambient noise hits your ear, that microphone is then hooked into the headphones and it generates the outside noise but with opposite phase. So by the time the outside and this new signal hit your ear, it's cancelled out, which hopefully, if the thing works well, means that all that you hear is music. So that's a practical example of destructive interference. It has a microphone to listen just to the outside. It adds on top of the music you're listening to another signal, the phase-inverted outside that you're hearing. Whatever that bleeds through your headphones, when that matches with the same thing but that's been turned around, those components cancel each other. Since you've still got the music that's part of that signal, but it doesn't match either of those, that still makes it through, that's what you hear.

Let's talk about the quantum model. We'll talk about the end result first, then we'll talk about how we come up with the model for this.

As we were talking about for atom orbitals, the unique shapes of those orbitals are caused because you have exactly one nucleus. If you have a hydrogen molecule, now you've got two nuclei. So those two nuclei form a new set of boundary conditions, which means you get a new set of orbitals. The dots I'm going to draw represent the nuclei. One of these orbitals is going to be higher in energy than the other. The lowest orbital looks a little something like this: you've got electrons that are spread all across this, and most importantly, you have electrons between nuclei. In this phone cord demonstration I did the other day, what happened when we went up from one energy level to the next? What was created? A node is created. Exactly the same situation is going to occur here: as we go up one level in energy, we're going to experience a node. That means this other orbital has this kind of shape. Very importantly, that means we have no electrons between the nuclei. For this top example, we call this an antibond. Why? Because, if you put a node between the atoms, and you try to hold those atoms at this particular distance, that positive charge from the two nuclei, they're bumping into each other. So that's a higher-energy system than if this had never happened in the first place. This orbital is an antibond because the energy is higher than if the atoms had not interacted. This other one, the lowest one, that would be a bonding orbital. Why? Because when you put electrons between the nuclei, that drops the energy of the system. This orbital is a bond because the energy is lower than if the atoms had not interacted.

Wouldn't it be nice if we could model this using the atomic orbitals? The math behind "simple" atomic orbitals is not that simple. After doing all that work to understand atomic orbitals, wouldn't it be great if we could use them somehow? The answer is, yes, we can use them, and the answer is LCAO, which means linear combination of atomic orbitals. {AO is a very common abbreviation} What this means is that atomic orbitals are added and subtracted from each other, that's what linear combination means – addition, subtraction. AOs are added and subtracted in order to produce a new set of MOs, molecular orbitals.

How is it done in this case? The hydrogen has a 1s orbital associated with it. What if we were to take two different s orbitals that had the same sign of the wavefunction? If they were both the same sign, then no matter how much overlaps one atom to the other, those functions are going to reinforce each other. The total value is going to increase. When you overlap them, you end up generating something that looks just like that bonding orbital I generated above. The first picture above I drew was the end result, the real bond. This is a model that we're using that happens to produce an orbital that happens to match that kind of bond. What if we had instead of two orbitals that had the same sign, what if we took them as the opposite sign as each other? If we put them right on top of each other, there'd be nothing left. Perfect constructive interference. But, we're making a molecule, so they're not right on top of each other, so a portion of one orbital cancels out the other, but that means we're going to get this split orbital, just like what I had drawn up above; for emphasis, I'm going to write that node in between.

One question that you might ask is: "Wait a minute; how do you know it's going to be the same sign? How do you know which one's going to be plus, which one's minus?" You don't. And it doesn't exist, anyways. Again, the shapes of atomic orbitals depend on there being exactly one nucleus. We have two nuclei involved, so these atomic orbitals don't even exist. This is our way as humans on paper to come up with a reasonable description of this bond and antibond. It is not possible that the same orbital is adding and subtracting with itself. So don't worry about when this happens, this is what we do on paper. Exactly this same process of adding and subtracting orbitals is what we're going to do when we hit hybridization.

What type of bond and antibond have we made here? Sigma. If you draw a line through each of these orbitals, whether bonding or antibonding, and if we were to spin around on this axis, it doesn't matter how much you spin, it's not going to change at all, it's rotationally symmetric. Just like we have s, p, and d orbitals, the first three types of bonds are sigma, pi, and delta. This is all related by the fact that there are zero, one, and two nodes in s, p, and d orbitals, and there's zero, one, and two nodes in the bonds, for sigma, pi, and delta. {Note to be care with sigmas and deltas} A sigma looks like a circle with a line coming off of it; a delta looks more like a lazy d. This is a sigma bond. This is a sigma star bond or an antibond.

How does this help us predict that hydrogen will form, but helium won't? What we normally do is create a diagram that looks like this: we put the atomic orbitals that we're going to use in our estimations on the sides. In the case of hydrogen, it's a 1s orbital. In the middle, we show the interactions we think are going to form with the sigma bond and antibond. We have one electron each on each hydrogen to start with. Molecular orbitals follow the same filling rules that atomic orbitals do. When these atomic orbitals disappear, we have to have somewhere for the electrons to go, they're going to go in the lowest-energy orbital first; Aufbau principle. Since there's only two electrons and the Pauli exclusion principle tells us we can squeeze two electrons into the same orbital, as long as they're the opposite sign [of spin], then this is the end of the story for hydrogen. The electrons fell in energy. That release of energy is favorable; that's why the bond forms. That's why the bond forms; that's why the molecule hydrogen form.

Why does that change when we look at helium? Helium's got the same 1s atomic orbitals to start with. Again, we're going to form a sigma bond and antibond, but this time, we have four electrons total that we're dealing with, two from each hydrogen. Aufbau principal again says the lowest orbital fills up first. Pauli exclusion principle says you can't put more that two electrons in, so the other two electrons have to go somewhere: they have to fill up that antibonding orbital. To not get bogged down in exact energy values, there's a quick calculation we can do that works in terms of describing the type of bond; that calculation is bond order. Bond order is defined as the number of bonding electrons, minus the number of antibond electrons, that whole thing divided by two. In the case of hydrogen, two bonding electrons, no antibonding electrons, so $(2 - 0) / 2 = 1$; we get our single bond. In the case of helium: two bonding, two antibonding; $(2 - 2) / 2 = 0$; no bond. This quantum model that takes into accounts waves, and therefore predicts antibonds, can be used to describe why helium doesn't form. Each antibonding electron causes a destabilization (increase in energy) that negates the stabilization (decrease in energy) provided by a bonding electron.

Sigma bonds don't just happen between s orbitals. The easiest case to describe is a sigma bond made by s orbitals, but it doesn't have to be.

The next case is when we have elements that more more that s orbitals [in their valence shell]. I'm going to use oxygen as my example. In this topic of diatomic molecules, there are some complications in there. If I chose to use boron or carbon versus oxygen, the order of the energies of the [molecular] orbitals flips around. For this class, we're not going to use these diatomic models again, because we're never going to have diatomic molecules, except for oxygen, or hydrogen, or nitrogen, that we ever encounter in o-chem. The one and only reason for me to show this is to see what a pi bond is. A pi bond results from this kind of situation: diatomic oxygen. Which row of the periodic table is oxygen on? The second row, so what kind of atomic orbitals are there available in oxygen [in the valence shell]? 2s and 2p. {SMOG for orbitals for oxygen} Right away we can see that we're going to have two p-orbital interactions: one is where these orbitals are directly in line with each other. That means, that's going to form a sigma bond, because if you drew the line all the way across and rotated it, that shape of that orbital wouldn't change. So that set of p-orbitals is going to make a sigma bond. But then we have another set of orbitals that, because of their proximity, do overlap ... but they don't directly overlap, it's this parallel overlap; that's going to create this other type of bond.

Just like we did for the sigma bond, we're going to have two ways that we can combine these p-orbitals. Again, it's not that two p-orbitals are able to interact in these two different ways; this is our way of adding and subtracting equations on paper to get these molecular orbitals. So one case will be when the p-orbitals do have the same sign, which if they do we get this kinda strange-looking shape. There is a node there, but this node is only caused because we're using p-orbitals which themselves have a node through them. This means we'll still have electrons between the atoms, no node between atoms; therefore, it's bonding, and we call that a pi bond. So sigma bond, no node through atoms or between atoms. Pi bond, one node, through the atoms. What about this other case? That would be if we let the p-orbitals be opposite phase. Again, you don't even have to worry how they're going to be opposite, cause we make them opposite in our model. If you combine them, you're going to have destructive interference; the phases cancel each other out, at least to the extent they overlap with each other. This orbital has this shape to it. There's still that original node because there's p-orbitals that we used. But now there is a node between the atoms. Exactly the same story applies here that we had for the sigma bond case: because electrons are now not between atoms, the positive charges are exposed to each other, and energetically that's not favorable.

Another way you could say it is: if you notice that the electrons are on the outsides of the molecule? Well, plus is attracted to minus, the nuclei would want to follow the electrons and move away from each other. Since we're trying to describe something in which the position of the nuclei are fixed, that means it takes energy to keep them there, so that's why it's an antibond. We designate that pi star.

To complete the picture for oxygen, just like on hydrogen, we start with the atomic orbitals being used on the outside, and the new molecular orbitals formed on the inside. We have the 2s orbitals, and the 2p orbitals. One set of those p-orbitals has a head-to-head overlap, so it's going to form a sigma bond. The other two sets of p-orbitals, those both have parallel overlaps, so those are pi bonds that form. Wherever you form a pi bond, you form a pi antibond as well, and where you form a sigma bond, you'll form a sigma antibond. What I was referring to as the complexity of this model is that, depending on whether you have carbon or oxygen or fluorine, the order of the sigma and pi bonds or antibonds can change.

There are six valence electrons total for each oxygen, so we have a total of twelve electrons we need to stuff into this diagram. So Aufbau principle, we fill the lowest orbital first. Next one up, next one up, and now here's where Hund's rule comes in. Because if we had only eight electrons somehow, if this was beryllium we were describing, then we would have one electron in each of those orbitals, but since we have more electrons, we'll then pair up. {Filling diagram} Doing a bond-order calculation, you can see we have eight bonding electrons, and we've got four antibonding electrons. $(8 - 4) / 2$, so this model would predict a double bond for oxygen, which that's exactly what oxygen exists as, as a diatomic molecule, a doubly-bound system.

We've seen that we need to use a quantum model to describe bonding because there is such a thing as antibonding. A bond is any time two orbitals interact and they made a new orbital that's lowest in energy, and an antibond is any time that two orbitals interact and you create an orbitals that's higher in energy.

{About pi antibond} It's that node that cuts from top to bottom that's critical here. That's why the nuclei are exposed and that's why it's an antibond?

{About diagram} The number of orbitals that you generate is equal to the number of orbital that you start with. {About sigma bond from p-orbitals} Here's not a node now but just an axis. One set of p-orbitals would overlap with the same sign. Because it's still symmetric in this way, that's why it's a sigma bond. The white region is where no electrons exist; empty space.

%If this model predicts that there's a sigma bond, two pi bonds, and a pi antibond, how can you describe the bonds that really exist there? My guess that since the energy of the pi start electron more closely matches that of the pi electrons that you'd effectively have a sigma bond and a pi bond. For organic molecules, any time you have a double bond, it will always consist of a sigma bond and a pi bond on top of it.

Hybridization

Here's the example I always use to explain why we need hybridization – methane (CH₄). We can draw a structure of methane like this, a very simple tetrahedral structure. What's the average bond angle between any of these carbon-hydrogen bond? 109.5°. Now let's draw out the atomic orbitals for carbon. Carbon is in the same row as oxygen, and even though it's electron configuration is 1s²2s²2p², even though there might be electrons in two of the p-orbitals at any one time, all three p-orbitals still exist. What is the angle between any two p-orbitals. If you had one and only one electron in an atom, then within a shell, all of the subshells inside are equal in energy. s is equal to p is equal to d. As soon as you have a polyelectronic system where you can start having interference between electrons, then, the orbital split, they become non-degenerate, they're no longer equal in energy. s orbitals in real atoms are not the same energy as p orbitals, that's why s orbitals fill before p.

Now look at this. Before, we have methane, which has four equal bonds, four, therefore, equal-energy bonds, and 109.5° angle. We see the atomic orbitals for carbon, however, are 90° angles to each other, and they're different energies. How in the world can we use these atomic orbitals to describe what's going on in methane? The simple answer is, you can't, because these orbitals don't even exist (because the shapes of the atomic orbitals depend on having exactly one nucleus). We have more than one nuclei, we have five different nuclei. So those five nuclei are all competing for electrons, so no way is it going to match what you get from atomic orbitals. So that's where hybrids come in. We saw above how we estimated bonds by adding and subtracting orbitals from the opposite atoms. Even before we allow bonding, what we do for hybridization is to say: let's take the atomic orbitals from the same atom, and add them and subtract them with each other.

Because of the internal mathematical structure of the atomic orbitals, when you add atomic orbitals together, they're just going to happen to create trigonal planar, tetrahedral, trigonal bipyramidal ... all of these different shapes, the orbital geometries will end up matching it in what would almost appear to be a magical way. The atomic orbitals of carbon cannot directly be used to describe the molecule methane since the geometry of the orbitals is incorrect and the energies of the different orbitals are not the same. To describe methane, a set of hybrid orbitals is created by adding and subtracting atomic orbitals on the same atom (LCAO).

classical bonding model
quantum bonding model
sigma & pi bonds

This classical model of bonding is able to describe H₂ but it fails to describe He₂ because it treats electrons as particles and does not take into account their wave behavior.

This orbital is an antibond because the energy is higher than if the atoms had not interacted.

This orbital is a bond because the energy is lower than if the atoms had not interacted.

LCAO – linear combination of atomic orbitals – atomic orbitals are added and subtracted to produce a new set of molecular orbitals (MO)

Each antibonding electron causes a destabilization (increase in energy) that negates the stabilization (decrease in energy) provided by a bonding electron.

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