

Lecture 4A • 10/03/11

One thing that can be confusing is: ok, there's this thing called a bond and that helps the molecule out. And then there's this thing called an antibond that destabilizes the molecule. How can you have a bond and an antibond? Isn't the antibond always there? There are bonding and antibonding orbitals, I want to emphasize, and so the spaces are always there. Just like in any atom, you have all these different atomic orbitals that could be filled. Whether or not something is going to be stabilized or destabilized is going to depend on how many electrons there are. In the hydrogen molecule, there is an antibonding orbital, but it's not full. There's only electrons in the bonding orbital, and that's why the molecule forms. In the case of helium, now you have electrons that occupy the antibonding orbital, which that's what's going to cause it to become destabilized, which that's what causes helium diatomic not to form.

A brief review of VSEPR theory

VSEPR stands for valence shell electron pair repulsion. The name itself is somewhat self-explanatory. Valence shell – why is that important? Because the valence shell contains the most energetic electrons, the ones that are going to participate in bonding. As far as electron pairs are concerned, for most of the molecules we're going to encounter, their electrons occur as lone pairs or as bonding pairs. It's a much rarer case that we're going to have individual electrons. In fact, those individual electrons aren't going to appreciably affect geometry or hybridization. Electrons tend to occur in either lone or bonding pairs. The repulsion portion of this is the fact that like charges repel. To put these pieces together, the shape of a molecule is predictable based on how many electrons are trying to get as far away from each other as possible.

Although there are quite a number of molecular geometries, we only care about a very limited number of shapes in organic chemistry. We're almost always going to be limited to carbon, oxygen, nitrogen, things that are in the first two rows of the periodic table, so rarely would we need something that could handle more than four bonds or lone pairs attached to a central atom. Let's look at some example molecules. If beryllium hydride existed, for example, that we only have two pairs of electrons that are in bonds that would be doing any form of repelling. If you only have two objects in three dimensional space, then how can you get two objects as far away from each other as possible? If they're at 180° or linear. If you have linear geometry, you're going to have those two pairs of electrons as far away from each other as you can get.

Hybridization is determined by geometry, not the other way around. When we do hybridization, we're doing that to create a new set of orbitals that matches the geometry that we see. Once you've figured out the rules for VSEPR theory, figured out the rules for geometry, they're the same rules we're going to figure out hybridization. So when you see linear, that's nearly always going to mean sp hybridization in practice.

Borane. That -ane ending means just single bonds and, in this case, it means boron with just single bonds to hydrogens. Very reactive compound. Why could we guess that it's very reactive? It's not just that it doesn't have lone pairs. It doesn't satisfy the octet rule; it can't, not as a neutral molecule. Boron, being so [high] on the periodic table, means those electrons, if you were to put them on, would go into very low energy levels. Lots of energy being released. This thing would burst into flames if you squirted it out into open atmosphere. Because it only has the three bonds, what's going to be the bond angle between them? 120°. Take a circle, chop it into thirds. $360/3 = 120$. What shape name do we assign to this? Trigonal planar. You've got to say the planar part, cause there's multiple trigonal shapes. Most of the time that you have trigonal planar geometry you're going to have sp² hybridization.

There's one more prototype shape – shapes that are generated when you only have bonds and no lone pairs. What is the standard bond angle in methane? 109.5°. We've already established a geometry name for this; what is it? Tetrahedral. Objects with tetrahedral geometry tend to have sp³ hybridization. These three shapes are formed in cases where there are no lone pairs. When lone pairs are present, they will distort the geometry slightly, since lone pairs have slightly more repulsive force than bonds. That's because in a bond, you've got a nucleus at bond ends, but in a lone pair case, you've got nothing else capping the other side of it, so effectively that electron density is spread out a bit more, which means more repulsion. I call these first three shapes prototype shapes, because they're the "pure" shapes, those things only formed by bonds.

There are some other prototype shapes – trigonal bipyramidal, octahedral. There are some derivative shapes – shapes generated by the presence of lone pairs – that we need to know. Both of these are going to be derivative shapes of a tetrahedron. The first example molecule is ammonia, which, if you imagined an axis coming off of that lone pair, it is related to tetrahedral geometry. But it doesn't have 109.5° angle like a tetrahedron does. What is the typical bond angle in something like ammonia? More like 107°. The geometry for this would be what? Trigonal pyramidal. It is slightly distorted, but it is still going to have sp³ hybridization.

Ammonia is different from ammonium. Ammonium is the ion. When you have just this -ia ending, that's the neutral compound.

Derivative shapes – shapes formed due to the distortion of lone pairs

The last of our derivative shapes is for water. Pretending again that we had axes at the positions where the lone pairs are coming off at, we can again make something that looks like a tetrahedron, but that “hedron” root means something that’s got all equal sides, angles, vertices, everything else. Since this is distorted, we can’t call it a tetrahedron any more, and it doesn’t make sense to, either, because you’ve only got two bonds, not four. You’ve only got two things that you’re getting a relative geometry between. What is approximately the bond angle in that molecule? 105° . We call this shape bent. Because this is a derivative of tetrahedron, because there are four pairs of electrons that need occupying somehow, we do call this sp^3 hybridization.

{review for the quiz}

Hybridization

Explain how the molecule methane demonstrates why hybrids are needed. What are two problems with using atomic orbitals to describe the geometry in methane? If you have four equal bonds, you need to have equal-energy orbitals, and s and p orbitals in polyelectronic systems are not equal. What’s the other issue? The shape is tetrahedral, but in carbon, the orbitals are at 90° angles to each other. So we have a geometry problem and we have an energy problem.

Hybrid orbitals, we create in order to explain bonding in polynuclear systems. When you have a molecule like methane, why is it that the s and p orbital won’t work, can’t work? Because they’re not there. What causes the unique shapes of atomic orbitals? The presence of exactly one nucleus. If you have multiple nuclei that all interfere with that electron, they’re not going to have the same atomic orbitals, the same orbital shapes any more. We need a way to describe what’s going on. Fortunately, because of the way that orbitals are structured, because of the functions involved, there’s these wild geometric coincidences that occur, where if we add and subtract atomic orbitals, we’re going to make orbitals that have linear geometry, trigonal planar geometry, tetrahedral geometry, it just happens that way.

Hybridization is LCAO – linear combination of atomic orbitals, which means that atomic orbitals from the same atom are added and subtracted in such a way to create a new set of orbitals that are equal in energy and match the geometry of the system. Atomic orbitals cannot describe molecules since molecules have multiple nuclei, and the shapes of the atomic orbitals are formed by the presence of only one nucleus. This why we need hybrids and what hybrids are. They’re fake. We create them on paper. Because we create them on paper, we do it in a way to match geometry. Hybridization is determined by geometry. More specifically, it’s determined by the number of lone pairs and sigma bonds. What about the pi bonds? If you imagine the p orbitals as being oriented, point up and below an atom, and p orbitals overlap sideways to make a pi bond. If they’re overlapping sideways, then that electron density is not between the two nuclei, so you’re not going to experience the same kind of repulsion you would by bonds and other things that are coming straight from the nuclei.

Let’s briefly look at how hybrids are formed. Let’s say that we needed two bonds to have 180° geometry in a linear system. What could we do to create two hybrids that have 180° geometry? We take an s orbital and a p orbital and add them together. There two different ways we can add them together, because of the signs of the wavefunctions involve. One possibility is that the phase of the s orbital happens to match the righthand side of the p orbital. Another way to do it is so that the phase matches the lefthand portion of the p orbital. You might ask: how do you know which one’s going to happen? That’s not a question you have to even ask, because it doesn’t happen because this is our fake way of doing it. We do it like this on purpose because it will generate two exactly opposite orbitals.

There is a deeper – albeit mathematical – explanation. These different orbitals are like coordinate systems. Just like in three dimensions, if you’re going to have a proper coordinate system, those three dimensions have to be completely orthogonal to each other. So x, y, and z: you can’t do anything to x to turn it into y or z, except for some kind of transformation. Same thing for r, theta, and phi. The reason r, theta, and phi makes a coordinate system is because those directions are mathematically orthogonal to each other. Atomic orbitals are mathematically orthogonal as well. What we’re doing is adding and subtracting in two completely opposite ways that will generate a new set of orthogonal orbitals. The number of orbitals that you generate is equal to the number of orbitals you start with. The number of hybrids generated is always equal to the number of atomic orbitals used, which is equal to the number of lone pairs and sigma bonds.

What are we going to generate when we add these things together? In the bottom case, we’re going to end up with a lopsided orbital where the lefthand lobe is larger, and in the top case we’ll end up with something that’s similar, where one lobe is larger than the other.

Are the hybrids molecular orbitals? They are and they aren’t. They are made up of atomic orbitals to make bonds and other molecular orbitals.

What would happen if I took these [orbitals] and wrote them simultaneously? You'd end up with something that looks like this, where you have the two different hybrid orbitals, and they each have these little tails, and they have 180° angle between them, which is exactly the angle that we need in a linear system. That's why we use sp hybridization. We did that because we took an s and a p and we added them and we made an sp hybrid. The what you do is add and subtract orbitals. Are we going to do this addition and subtraction for all possible hybrid orbitals? No, cause it gets nasty for anything but a linear system. You'd look at what coefficients you'd put in from of each of the orbitals and create a matrix of them and then make all unique combinations.

What's the practical side? If we need trigonal planar geometry, that means we need three bonds that have to be equal-energy, so we need three atomic orbitals to make those hybrids. So we take an s , a p , and a p orbital, the lowest three energy orbitals in the valence shell, then that makes sp^2 hybridization. If we have four bonds, then we need four orbitals, so it'd be $s p p p$, so it'd be sp^3 hybridization.

Let's see some examples, and then we'll come up with a rule for hybridization. What we're going to see now are these things I lovingly call structural molecular orbital graphs, in other words, SMOGs. This is a diagram that represents the kind of orbitals, not the phase of orbitals. These diagrams depict the kind of orbitals present, not the phase, to demonstrate the structure of a molecule. Methane, CH_4 , has four bonds, which means we need four hybrids, which means we're going to use $s p p p$, which means it's sp^3 hybridization. If it's sp^3 hybridization, how many of these hybrid orbitals do we have? Four of them. Here's what the SMOG looks like. {I try to color-code the SMOGs to be consistent; black – s ; purple – sp^3 } I've done a couple of things here in this diagram. I've simplified the hybrids, so instead of showing over and over again that they do have nodes in them – one lobe, one portion of it was much larger than the other – instead of showing that split orbital every time, I'm just showing the major lobe. So, for simplicity sake, only the major lobe of hybrids is being shown. The other thing that I've done here is that I've also put all for hybrids simultaneously into the diagram. But that's what these diagrams are for: to show the geometry, to show the types of orbitals present.

How did I figure out what type of hybridization did I have? It was because I knew it was tetrahedral, because there were four different bonds. If there's only four bonds that need to have their electrons be occupied somewhere, I need four orbitals of some sort. But they need to be four equal-energy orbitals, which is what hybridization provides us. If we were to look at the $2s$ versus $2p$ orbitals of carbon, we've taken these unequal-energy orbitals and, now, we've made equal-energy sp^3 orbitals. So hybridization solved our geometry problem, and it solved our energy problem as well.

[The diagram from last lecture] is a molecular orbital energy diagram. So there's two types of diagrams that we'll be using this quarter. One is exactly what we did last time, where you show the energies and the filling patterns for the different molecular orbitals, and that's a molecular orbital energy diagram. This is a structural diagram. This is to show what a molecule looks like, because this is how we're going to explain how molecules react. Imagine, for example, if we had a p orbital that was next door to one of these sp^3 orbitals. Imagine that I took this hydrogen off and put some other portion of a molecule here where there's a p orbital sticking out. That p orbital can overlap with one of these neighboring sp^3 orbitals. That small amount of interaction is something known as hyperconjugation. It's one way of explaining why, if you have three carbons attached directly to this, it may or may not be as reactive as if you only had two, or if you only had one. That's why you need to know these structural pictures, because that's the only way we can talk about these types of within-molecule interactions.

You don't have to have equal-energy orbitals to form a bond, but we know that methane has four-equal energy orbitals, four equal-energy bonds. We know the atomic orbitals of carbon are not equal, so that's why in whatever story we tell, whatever model we use to explain bonding in methane, we can't use atomic orbitals, because they don't match real-life observations, they don't match the fact that the energies are equal. But once we hybridize them, then they average out. They become equal energy, so then they're suitable for describing methane.

But energy is needed to bump a $2s$ electron up to a $2p$ orbital. But, the total energy these two cases is the same, it's just now that it's distributed equally in the hybrid orbitals.

The next example I want to do is CH_3^- . How many pairs of electrons are around carbon in CH_3^- ? How many electrons total around around carbon in CH_3^- ? There are eight, because the way CH_3^- would be formed, if you pulled a hydrogen off of methane and left the electrons behind. If you have a neutral molecule and you break a bond, if you break it unevenly, then one atom has to become positive and one atom has to become negative. If you had four bonds to carbon, that would make a neutral carbon. When you put one more electron effectively on carbon, that's what makes it negatively charged. So CH_3^- is this molecule: three bonds and a lone pair. What is the geometry? It's the same as ammonia: trigonal pyramidal. It is not tetrahedral, since that lone pair causes distortion; but it's still a four-object shape. The difference between a lone pair and a bonding pair is so small, either one would count towards hybridization. So, four hybrids are still needed, which means you're still going to use four atomic orbitals, which means this is also going to be sp^3 -hybridized. if we wanted to draw a picture for this molecule, the only difference is that there are only three hydrogens present. So one of the sp^3 orbitals, you would just show as being bare. In real life, we know that this change is subtle, 109.5° versus 107° , not the hugest change in the world.

Where we get a huge change is if we do the molecule CH_3^+ . What would that shape have to be? What would that molecule in a Lewis dot structure look like? To generate a plus charge on carbon, you'd have to take a bond away from methane and leave nothing behind. Carbocation means a cation located on carbon; it's a slight shorthand. Up above, we had a carbanion, which means an anion, which is a negative charge, on carbon. Does a positive charge figure into VSEPR theory at all? No, because VSEPR theory is about negative charges, so the fact that you've got a positive charge there doesn't mean anything. So, only three hybrids are needed, because there are only three bonds, which means it's going to be sp^2 hybridization. What does that mean? If we look at the s and p orbitals that we start with, we're going to end up with this situation (remember that we're taking one electron away in this example). We'll have the sp^2 orbitals. When I say sp^2 orbitals, how many of them are there? Three. Why? Because that's how many we needed. We took three atomic orbitals in the first place cause we wanted to make three hybrids because we had the three bonds that were all equally-spaced from each other. But look what's left: a p orbital! But wait, supposedly there's no such thing as atomic orbitals in molecules, so why are you showing me a p orbital? Because it works. Cause it describes how a molecule behaves well enough that that's why we use this model. It's just a model. But we have to reflect that in our diagram, because this p orbital would effectively be the site where a new bond would form. This plus charge that we just formed, would with something that's negatively charged react at the site of the p orbital. So the SMOG diagram for this molecule would look like the following. {blue for sp^2 , red for p orbital} It's that leftover p orbital that's most frequently forgotten.

The next example is CH_3^\bullet , which that's our first case of having a radical, a molecule with an unpaired electron. What would the Lewis dot structure for this look like? To make carbon neutral, it effectively has to have four electrons in its valence shell, which according to formal charge we could get if we left just a single electron on carbon. But single electrons do not have the repulsive force of a pair of electrons. So, other than a 1% deviation by having an electron there, lone unpaired electrons have no effect on geometry. If they have no effect on geometry, they have no effect on hybridization. Lone electrons do not have the repulsive force of lone, or bonding pairs, of electrons. Therefore, single electrons do not affect geometry, so they do not affect hybridization. So, this has a nearly identical diagram to CH_3^+ , the methyl cation. This methyl radical looks structurally identical.

This brings us to one of the most interesting cases so far: this diradical. What's that going to look like? If we drew a more complete Lewis dot structure it would look like this. What is the hybridization of each carbon in this molecule? We just saw in the previous example that a radical is not counted in hybridizations. So when we had just three bonds, that was trigonal planar geometry. Same thing for each carbon, individually, is going to happen here. Each carbon, on its own, only has three bonds, so each carbon is sp^2 hybridized. What would a diagram for this look like? You'd have a sp^2 -hybridized carbon on the left and a sp^2 -hybridized carbon on the right. I've already drawn in one of the p orbitals, but here's an important point. This other p orbital I'm about to draw in, if I drew the same direction as the first orbital, what would that end up making? A pi bond. This is my backwards way of showing why pi bonds do not affect geometry. If you had each radical individually If you had a pi bond, you could say that each atom has a radical. Well, radicals don't affect geometry, that's why double bonds don't show up in VSEPR theory. The only way you can draw this is if the p orbitals were perpendicular to each other. So if you were looking at this from the side, looking at it from a side perspective, the p orbitals must be at 90° angle to each other.

VSEPR – valence shell electron pair repulsion

The valence shell contains the most energetic electrons – the ones that participate in bonding
Electrons tend to occur in either lone or bonding pairs
Like charges (such as electrons) repel

The shapes of molecules are generated by electrons trying to get as far away from each other as possible.

These three shapes are formed in cases where there are no lone pairs. When lone pairs are present, they will distort the geometry slightly since lone pairs have slightly more repulsive force than bonds.

Derivative shapes – shapes formed due to the distortion of lone pairs.

Hybridization

LCAO – atomic orbitals from the same atom are added & subtracted in such a way as to create a new set of orbitals that are equal in energy and match the geometry of the system.

AOs cannot be directly used to describe molecules since molecules have multiple nuclei, and the AOs are formed by the presence of one nucleus.

Hybridization is determined by geometry – determined by # of lone pairs and sigma bonds

How hybrids are formed

The # of hybrids generated is always equal to the # of AOs used.

Structural Molecular Orbital Graphs – SMOGs

These diagrams depict the kind of orbitals present (not phase) to demonstrate the structure of a molecule.

CH₄ – 4 bonds – 4 hybrids – s, p, p, p – sp³

For clarity, only the major lobe of hybrids is being shown.

4 hybrids are still needed – 4 AOs – sp³

carbanion – an anion (– charge) on carbon

carbocation – a cation (+ charge) on carbon

only 3 hybrids are needed because there are only 3 bonds – sp²

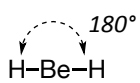
radical – a molecule with an unpaired e[–]

lone electrons do not have the repulsive force of lone or bonding pairs of electrons. Therefore, single electrons do not affect geometry, so they do not affect hybridization.

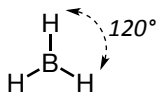
p orbitals must be @ 90° to each other

Structures

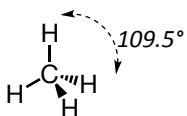
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beryllium hydride
linear
sp

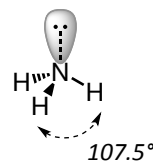


borane
trigonal planar
sp²

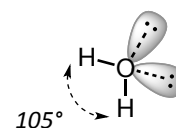


methane
tetrahedral
sp³

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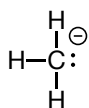


ammonia
trigonal pyramidal
sp³



water
bent
sp³

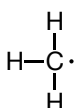
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