

## Lecture 4B • 10/04/11

We're going to start a brief review of VSEPR theory. We're going to focus on the shapes that we normally use for organic molecules. After that, we move on to hybridization. That's going to be our way that we come up with structural pictures of what organic molecules look like. That's what this structural molecular orbital graph refers to – a diagram of what a molecule looks like. Then, we'll apply these principles of hybridization to a set of common organic molecules.

Let's start with VSEPR. What does VSEPR stand for? Valence shell electron pair repulsion. To break that phrase down, first focusing on the valence shell: the valence shell is where the most-energetic electrons are. So those electrons that participate in bonding – and therefore are going to have an influence on molecular shape – those are the valence electrons. The valence shell contains the most energetic electrons, the ones that participate in bonding. What does the electron pair have to do with anything? Electrons tend to come in pairs – either as lone pair electrons, or as bond pairs of electrons. Individual electrons – something that might be found in a radical – don't have the repulsive force that a pair of electrons has. As far as determining shape – and shape determines hybridization – only pairs of electrons are what we worry about. Electrons tend to occur in either lone or bonding pairs. The last part of this – the repulsion part – is the fact that we have all of these similarly-charged objects. Like charges repel, so the repulsion of these different valence electrons – whether they're distributed as bonds or lone electrons – that repulsion is what's responsible for the shape of a molecule. Like charges, such as electrons, repel. The fact that they are the most energetic are why they're the ones that are most reactive. The shapes of molecules are generated by valence electrons trying to get as far away from each other as possible.

Let's see a small collection of molecules where we can talk about these fundamental shapes. These first three shapes that I'll present are what I refer to as prototype shapes – they're the main shapes that you get from molecules that only have bonds, no lone pairs. The three that we have to worry about for organic chemistry, we can demonstrate with beryllium hydride, borane, and methane. In beryllium hydride, since we only have two bonds, two pairs of electrons, what, geometrically, is the best way to get those pairs of electrons as far away from each other as possible? What kind of shape should we expect? Linear. In three-dimensional space, the furthest that two objects can get away from each other is to be  $180^\circ$  apart. That is the bond angle that we should observe in this kind of system, and the shape is called linear. Usually, when we have linear geometry, we're going to have sp hybridization.

For borane – very, very reactive molecule. Can anyone think why borane might be unusually reactive? How many does [boron] have in its valence shell? Total, because of the bonds? How many electrons in a bond? 2. So if you see three bonds, how many electrons do we have? 6. But the octet rule tells us that we'll have something that's stable if we have 8 electrons. So if you squirt this stuff into open atmosphere it will burst into flames because of how violently it will react with lone pairs in oxygen or ammonia or whatever happens to be in open atmosphere. Lacking that octet, that's why it's so reactive. Because it only has the three bonds, what kind of shape and what kind of bond angles do we expect? Trigonal planar. The planar part of that name is super duper critical, because we have trigonal planar, trigonal pyramidal, and trigonal bipyramidal as three valid shape names; so you can't ever just say trigonal, you have to emphasize that it is trigonal planar. Because it's trigonal, it's got  $120^\circ$  angles. Generally, when we have trigonal planar geometry, we're going to find that we have sp<sup>2</sup> hybridization.

Then the last shape – methane. What shape does methane have? Tetrahedral. It's a perfectly-balanced shape, which is why it's a hedron shape. In tetrahedral geometry, what is the bond angle that we'll find?  $109.5^\circ$ . Generally, with tetrahedral geometry, we have sp<sup>3</sup> hybridization.

These, again, are what I call prototype shapes because everything is symmetrically balanced. What happens, when we now introduce lone pairs into one of these molecules? What's going to happen? It's going to push the bonds out more because it wants more space. Lone pairs end up having more repulsive force because they only have one nucleus that's associated with them. So yes, it's going to cause a distortion of these shapes, so you wouldn't, for example, have a perfect tetrahedron any more. When a lone pair is present, it causes distortion of the molecular geometry, due to the fact that lone pairs have more effective repulsive force than bonding pairs of electrons.

So we have a series of what I refer to as derivative shapes. You may encounter the opposition of the terms electron pair geometry versus molecular geometry. The distinction between these types of geometry – one way to approach the molecule is to just look at how many pairs of electrons there are, because these distortions caused by lone pairs are really small in comparison to the repulsion of the different lone pairs themselves. So we're going to see trigonal pyramidal and bent as variations of the tetrahedral geometry. So electron pair geometry just refers to the prototype shapes generated according to whether you have two pairs, three pairs, four pairs, five pairs, or six pairs of electrons. I want you to know what the real, end-result shapes are. I classify these as prototype, meaning no lone pairs, or I call the other ones derivative shapes.

Let's look at the two derivative shapes we care about. The first example molecule is ammonia. Ammonia, with an -a, is the neutral molecule NH<sub>3</sub>; ammonium, with the -ium ending, that's a cation, NH<sub>4</sub><sup>+</sup>. We're going to do the neutral molecule ammonia, which as a lone pair and then three bonding pairs of electrons.

If we imagine that the lone pair occupies the fourth place on a tetrahedron, we can see that this is almost a tetrahedral shape. But, no matter what you do, you're never going to get a bond to exactly balance out with a lone pair, so it's not totally symmetric. And, because the lone pair has more repulsive force as is going to push the hydrogens closer together, what's the average N-H bond angle in this molecule?  $107^\circ$ . And the name of this – trigonal pyramidal. Curiously enough, since it's only a minor perturbation of the geometry, we're going to find that this is still called  $sp^3$  hybridization.

The last shape, also a derivative shape, that's for water. We can imagine that the two lone pairs would provide what would otherwise have been a tetrahedral-like shape. But again, the lone pairs distort the geometry. It doesn't make sense to call it a tetrahedron if two of the bonds aren't really there. This is called a bent shape, with  $105^\circ$  bond angle between hydrogens. This is bent, and it's  $sp^3$ .

Any other shapes – octahedral, trigonal bipyramidal, see-saw, t-shape – probably won't encounter any of them this quarter.

If you have a radical, would it [a single electron] have the equivalent repulsive force as a bond? No

### Hybridization

In methane, all of the bond angles are equal, and all of the bond energies end up being equal, and they have this tetrahedral geometry with  $109.5^\circ$  angle. Compare that to the valence orbitals that would be available on carbon: those have different energies – the s and p orbitals are different in energy in polyelectronic systems – and  $90^\circ$  angles, which doesn't match the  $109.5^\circ$  at all. Why is it that we can't use these atomic orbitals to describe methane directly? If those are the atomic orbitals, what happens that somehow we end up with these  $109.5^\circ$  angles instead of  $90^\circ$ ? What is the reason that these orbitals simply aren't there? The root cause of all of this is that atomic orbitals only exist in atoms, not molecules, because the shapes of atomic orbitals are generated by the fact that you've got one and exactly one nucleus. It'd be like if you have an old-fashioned television set, not a flatscreen, but one that used a tube. If you put a magnet on the TV, you're going to generate this color pattern that the colors all seem to flow around that magnet. Put a second magnet on there, and you're going to create a new set of patterns that revolve around both of those. Something similar happens with electrons. You put just one nucleus out there, you get one set of orbitals. As soon as you put another nucleus out there, we get bonds and antibonds; in other words, we get these new molecular orbitals. We can use atomic orbitals to estimate, we can use it as a model, but atomic orbitals can't work, because you have multiple nuclei.

This is the start: that atomic orbitals (AOs) cannot be used – directly, at least – to describe molecules, since molecules have multiple nuclei. The shapes of atomic orbitals are formed when only one nucleus is present. We're going to take the same approach that we took in bonding. In bonding, we took atomic orbitals from different atoms, added and subtracted them together, and came up with these new orbitals: sigma bonds and antibonds, pi bonds, pi antibonds. Before we even approach bonding, to give us a system of orbitals that have the same energy – which, ostensibly, that's what these shapes are telling us. VSEPR theory tells us electrons want to get as far away from each other as possible – one thing that's hidden in that is that they tend to be equal energy, because that's how they would be equally spaced from each other. These hybrid orbitals we create to make the geometry match and to equalize the energy, and we do this by adding and subtracting orbitals not from different atoms, but on the same atom. That's the difference between hybridization and bonding. Hybridization, we do this orbital creation first, and then after that, we worry about the fact that bonds are going to form. Hybrids are formed by adding and subtracting orbitals from the same atom – this is linear combination of atomic orbitals (LCAO) – to create a new set of molecular orbitals that are equal in energy and match the geometry of the system.

To make a pointed comment – geometry determines hybridization. Hybrids are fakes. We, as humans, are adding and subtracting orbitals on paper to come up with a reasonable model that works, which is why we keep on using it. But, because we're trying to match this system, that means whatever real-life geometry we have, establishes hybridization, not the other way around. Hybridization is determined by geometry, which in turn is determined by how many lone pairs and sigma bonds that you have. The number of hybrids needed is equal to the number of lone pairs plus sigma bonds – the number of unique ways in which electrons are distributed around a molecule.

If you took a picture of methane, you wouldn't see the  $sp^3$  hybrids. You'd see bonding orbitals that we model using these  $sp^3$  orbitals and the s orbitals, which also don't exist because they've made the bonds. We're only using this model because it matches real-life observation. Molecular orbitals, you cannot solve for exactly. You can only solve an atomic orbital if you have exactly one electron and one nucleus. Beyond that, we either make these statistical approximations, or, we start out with the atomic orbitals we can solve for and keep on manipulating them in such a way that it gives us something that matches observation.

{Example of ring of copper atoms trapping an electron the shape of the orbital of which can be imaged. Using crystallography to get molecular shape itself}

Even once we make these hybrids, we're making bonds, which means those hybrid orbitals have already mixed with another orbital and disappeared, because it becomes bonding orbital. You've just got this balloon shape of electron density floating in space, and that's what exists. Then we, as humans, try to understand it. We create one model – bonding – which is great for two atoms. But for methane, we can't just take atomic orbitals, the geometries don't match. Just like in coordinate systems: we can have x, y, and z as our orthogonal labels for a three-dimensional coordinate system, but we can also call it r, theta, phi. Those are three coordinates that are also mutually orthogonal to each other. That transformation is very much like what we're doing here. We start with a certain number of atomic orbitals (which, mathematically, they're also orthogonal) and we convert them by a matrix operation into hybrid orbitals.

Let's see some practical application.

How are the hybrids formed. Let's just see one example of that before we do our molecules.

If you had a linear system, for example, we need orbitals that have  $180^\circ$  geometry. We can make new orbitals like that if we chose to use an s orbital and combine it in certain ways with a p orbital. This is one of those places where sign of the wavefunction matters. If we're taking two functions, then wherever their sign is the same, that's constructive interference and you'll magnify the orbital at that place, or where the orbitals have opposite sign, mathematically, they'll cancel each other out, so the orbital will appear to shrink. Same type of argument happens here that happens in bonding: it's not that magically the orbitals are somehow able to add and subtract in just these ways; it's our way on paper of doing it. So we chose one sign or the other for the s orbital, and then we'll take the p orbitals and look at the two different cases of what their signs would be like if we combined it with this s orbital.

In one case, we're going to end up with a major lobe pointing in one direction, and in the other case it will be pointing in the opposite direction. If we wrote those two new orbitals simultaneously on top of each other, it looks something like this. You'd have the little back ends of the orbitals, but you'd have these two major lobes, and they would have that desired  $180^\circ$  geometry. The reason this happens somewhat magically is some of the mathematics buried in atomic orbitals. You take two of them like this and combine them, you're going to get  $180^\circ$  degrees. If you take three of them and combine them the right ways, you're going to get  $120^\circ$ . Since, in this example, we used a p orbital and an s orbital and combined them, what we came up with we call an sp orbital. You see one of the rules of combining orbitals, which is: the number of hybrids that you end up with is equal to the number of atomic orbitals that you start with. The number of hybrids that we need is, again, equal to the number of lone pairs and sigma bonds, the number of unique directions that we have pairs of electrons.

Methane, for example, had four bonds. Water has two bonds and two lone pairs. Ammonia has three bonds and a lone pair. But in all three cases, we've got four unique directions that things are pointed. Since we've got four orbitals, then, we're going to use four atomic orbitals, s, p, p, p. Combining these together, that's how we get sp<sup>3</sup>. Why do we have s and p? They're the lowest-energy valence orbitals available. We start with lowest energy first – the s orbital – and then each additional orbital we need, we take from whatever valence orbitals are available, which in the case of carbon, is going to start with the s and move to the p, then in other atoms, to the d.

These types of pictures that I'm going to start drawing are called structural molecular orbital graphs, or SMOGs. I came up with this name to distinguish them from molecular orbital energy diagrams. In molecular orbital energy diagrams, we saw two atomic orbitals interacting to make a bond and an antibond, and we drew the lines and filled in the electrons. This diagram we're about to draw shows the shapes of molecules, which is why I wanted to come up with a name for it, so that you know that you need to worry about energy versus shape. These diagrams show the kind of orbitals present, not phase. When I start coloring these things in, we're no longer talking about + and –, we're talking about s, p, d, sp<sup>2</sup>, etc., what kind of orbital is it. The reason to do this is to demonstrate the structure of a molecule.

I'm going to make a common simplification. If you look at how the hybrids are created, you'll see that the hybrids have nodes in them. They have a major lobe – the larger portion of the orbital – and this little bunny tail that's stuck in the back. To make the pictures a little bit clearer, I'm only going to draw the major lobe. This is a convention I'm going to follow, where I'm going to write simplified hybrids. Instead of writing the major lobe and the minor lobe, I'm just going to write the major one.

Our first molecule, methane. It has four bonds, four sigma bonds. That means we need four hybrids, which means we need four atomic orbitals, which means we use s, p, p, and p, and so we call it sp<sup>3</sup> hybridization. {colors} Methane I would draw like this. If we just have hydrogen that just has the one bond, does that mean we use just the s orbital? Yes, that's the way we model it. But wait, you just said that atomic orbitals don't exist in molecules? Yes, that is true also, but that's why we call it a model. Then, we'll have four sp<sup>3</sup> hybrids. The number of hybrids is always equal to the number of orbitals used. Since we used four, we have a total of four of these hybrids. That's the picture of methane.

Just a comment on energy. Before hybridization, we could have written something like this: that carbon would have had its 2s orbital and two of its 2p orbitals partially filled, but after hybridization, part of the point of hybridization is that all [four] of these sp<sup>3</sup> orbitals are going to be equal in energy. You're averaging the energies, so it's going to be in between the two. One set of orbitals disappears, we replace it with a new one, and the total energy of the two systems has to be the same.

Phase means plus or minus sign of the wavefunction. So, p orbital, half of it is negatively signed, half of it is positively signed. In these pictures, I'm not showing sign, I'm just showing shape.

What if we pulled a hydrogen off of methane and left the pair of electrons that used to be in that bond behind? What if we made what's called the methyl anion. To introduce a small bit of terminology, in general, any time you have a negative charge on carbon, it's called a carbanion. For the methyl carbanion, the way we would get that is by breaking a bond from methane, leaving the lone pair behind, which in terms of formal charge means there's now a negative on carbon. That negative charge is going to cause a distortion of the geometry, but it's 107° versus 109°. Since it's such a small difference, we're still going to use sp<sup>3</sup> hybrids to describe this. We have three sigma bonds and a lone pair, which again means we need four hybrids, which means we need for atomic orbitals, which again means we use s, p, p, and p, and so again we have sp<sup>3</sup> hybridization. The only difference in the diagram will be that we have a missing hydrogen. If a reaction happens where a hydrogen without its electrons is taken away, other than a small angle change, nothing much else changes in a molecule.

That's a completely different story than what would happen if we took hydrogen off of methane and we took the pair of electrons with it, leaving a positive charge on the carbon. That would be CH<sub>3</sub><sup>+</sup>, which is the methyl cation. There is a general term, carbocation, which is a cation, a positive charge, on carbon. In this case, only three hybrids are needed, because a positive charge is not an object, it's the lack of an object – the lack of [a pair of electrons]. Only three sigma bonds are present, which means we only need three hybrids, which means we're going to use s, p, and p because they're the lowest-energy orbitals, which means we end up with sp<sup>2</sup> hybridization. In this case, what will we have around carbon? Since we're missing an electron [pair] now, this is what our before picture would look like, when we hybridize, we'll have orbitals that are in between the s and p in energy, but we'll still have a p orbital left over. So, our SMOG for this system would look like the following. {color}

The important point here is that if you had a pair of electrons coming in to make a new bond with this thing that's now positively charged, the way we model that bond formation is to say the electrons get donated into this p orbital. Part of the evidence that this is a good explanation is that you can end up forming two different molecules, depending on whether it attacks from the top or the bottom. Both results, on a very small molecule like this, happen equally.

The last one today is a radical, to address this question of single electrons. Since individual electrons do not have the repulsive force of pairs of electrons, single electrons do not affect geometry, so they do not affect hybridization. In this example, CH<sub>3</sub>•, which is the methyl radical. It will have an identical structure [to the methyl cation]. Technically, you won't have 90° angles like the other, more like 89°, but close enough that we ignore that difference.

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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 valence electrons trying to get as far away from each other as possible.

Prototype shapes – shapes due only to bond

When a lone pair is present, it causes distortion of the molecular geometry due to the fact that lone pairs have more effective repulsive force than bonding pairs of electrons.

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

Hybridization

AOs cannot be used directly to describe molecules since molecules have multiple nuclei; the shapes of AOs are due to there being exactly and only one nucleus present.

– hybrids are formed by adding & subtracting orbitals from the same atom (LCAO) to create a new set of molecular orbitals that are equal in energy and match the geometry of the system.

– hybridization is determined by geometry – # of hybrids needed = # of lone pairs & sigma bonds.

How hybrids are formed

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

Structural Molecular Orbital Graphs – SMOGs

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

CH<sub>4</sub> – 4 bonds – 4 hybrids – 4 AOs – s, p, p, p – sp<sup>3</sup>

CH<sub>3</sub><sup>-</sup> – methyl anion

carbanion – an anion (-) on carbon

3 sigma bonds & lone pair – 4 hybrids – 4 AOs – s, p, p, p – sp<sup>3</sup>

CH<sub>3</sub><sup>+</sup> – methyl cation

carbocation – a cation (+) on carbon

3 sigma bonds – 3 hybrids – s, p, p – sp<sup>2</sup>

Since individual electrons do not have the repulsive force of pairs of electrons, single electrons do not affect geometry, so they do not affect hybridization.

CH<sub>3</sub>• – methyl radical

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Structures

Identical to those from lecture 4A (10/03/12)