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5.112 Principles of Chemical Science, Fall 2005  
Transcript – Lecture 25

Over on the side board here, I want to show you a few representation of the ethylene molecule that we were talking about at the end of last hour.

When you see representations of molecules that appear throughout your textbook, as well as in this class, I want you to see if you can recognize just what property of the molecule it is that is being represented. In this case here, we have arbitrary sized spheres that represent the two carbon atoms and the four peripheral hydrogen atoms. And then what I have plotted around it is a see-through representation of the electron density at a particular isosurface value of 0.1 electrons per unit volume. So, that is a representation. And we are going to be seeing a number of different kinds of representations, and you will need to be able to distinguish between them. And, in particular, we were talking last time about different kinds of bonds. We talked about sigma bonds that were cylindrically symmetric about the internuclear axis of the two atoms that are bonded together.

And we also talked about pi bonds. And I brought up the pi bond in connection with the ethylene molecule that we were just looking at, a different representation of. And so, now let me show you what a pi bond can look like. Here is a representation of the ethylene molecule. Again, I have arbitrary sized spheres that show us just where the nuclear positions are in three-dimensional space.

So, we are talking about the equilibrium geometry of the ethylene molecule. And what you see here is that if the molecule is lying in the xy plane then each of these carbons has a 2pz orbital that has a positive lobe and a negative lobe respectively above and below the plane of the molecule.

And so, normally, when we talk about atomic orbitals, we can reference their phase as either positive or negative. And we often, in representations like this one, associate the positive phase with one color, here blue, and the negative phase with a different color, here

yellow. I can choose whatever colors I want for those, but this is also a type of isosurface.

And it represents the in-phase side-to-side overlap of the positive above the plane lobes of the carbon 2pz orbitals and the negative lobes below the plane of the carbon 2pz orbitals experiencing side-to-side overlap. And so, you see the two electrons that could be paired up, spin paired, one spin up, one spin down in this pi bond are smeared out both above and below the plane

But there is no contribution at all to the electron density in the plane from an orbital like this. When we looked at electron density isosurfaces, as we have done a few times in this class, what we are looking at there is an isosurface corresponding to all of the electrons in the molecule. And here what we are looking at is an orbital that can house just two electrons, one spin up and one spin down, so we are focusing our attention on a function that involves just two electrons bonding in a pi bond that has, as a nodal surface, the plane of the molecule.

The plane that contains all six of these nuclei, the two carbons and the four hydrogens. We talked about nodal planes last time. And the issue of nodal planes, nodal surfaces is going to be very important in today's lecture. Let's go over here and start talking about hybridization.

On this board last time, I gave you kind of a timeline where we talked about contributions to different aspects of electronic structure theory for molecules by different people, some of who were recognized with Nobel Prizes, others who were not.

And one of those people, namely Linus Pauling who run two Nobel Prizes, not both in chemistry, came up with this idea of hybridization to solve one of the problems associated with atomic orbital nodes. And let me work on this and illustrate this to you by taking a pretty simple molecule that has only four atoms.

And this molecule is one that, in fact, we have seen before. It is an example of a Lewis acid, so any discussion of electronic structure of this BH<sub>3</sub> molecule better come out with a description of why it is a Lewis acid. But let me now point something out. That is, if I make the direction that coincides with this top BH bond, the x-axis.

And in the plane of the board, the y-axis perpendicular to it, as shown. And then, of course, the z-axis coming perpendicularly out of the plane

of the board. Linus Pauling recognized a problem. And let me give these hydrogens descriptors. I will make this one A, this one labeled B and this one labeled C.

And the problem is that we have a  $p_z$  orbital with one positive lobe coming out of the plane of the board up here. This would be where the blue lobe is. And the yellow lobe would be back behind the plane of the board analogous to the  $\pi$  bond that we just looked at up on the screen. And what you will see is I can draw it this way. I am rotating this planar  $BH_3$  molecule.

That allows me to draw the  $p_z$  orbital in a way that you can visualize. And the observation that I want you to take away from this drawing is it has to do with the relationship in space of the three hydrogen nuclei to an important property of the  $2p_z$  orbital.

What we can say is that these three hydrogens, A, B and C reside in the nodal plane of the  $2p_z$ .

They lie in the  $2p_z$  nodal plane.

That is, the  $2p_z$  on the boron. And the wavefunctions that these hydrogens bring into the problem of the electronic structure of the  $BH_3$  molecule are spherically symmetric. They are simple  $1s$  orbitals. And so, if you draw one of them here, remember that a  $1s$  orbital is spherically symmetric.

You can see that any positive reinforcement that would occur by overlap here is equal and opposite to the negative reinforcement that will occur down here. And this is something that is true whenever a hydrogen  $s$  orbital lies in a nodal plane. There is no net overlap--

--between the boron's  $2p_z$  and the hydrogen  $1s$  orbitals. When we try to describe the bonding in this molecule, we cannot have any bonds that involve  $2p_z$  and any of the three hydrogen  $1s$  orbitals because there is no net overlap between them.

Because those spherically symmetric orbitals lie in the nodal plane of  $2p_z$ . And that means further that we need to form three in-plane bonds.

And that is the  $xy$  plane in plane bonds.

And these three bonds must be equivalent.

And what is interesting about the fact that they must be equivalent is that what are the three orbitals that the boron has that are in the xy plane, the three valence orbitals?

There is the 2s, the 2px and the 2py. Three orbitals that are not identical to one another, yet we need to make three identical bonds because all the studies that we do on the BH<sub>3</sub> molecule tells us that each of these bonds are the same length, the molecule has the perfect symmetry of a Mercedes Benz symbol, its trigonal planar.

It has this three-fold rotational symmetry to it. And so somehow, using a 2s, a 2px and a 2py, we need to make three equivalent bonds. This is an energy level diagram. And so, Pauling came up with the idea of promotion. And promotion will correspond to the following. I can draw 2px, 2py, 2pz and 2s.

And I can populate with electrons. The boron atom has three. Now I have put in three electrons into this energy level diagram for the boron atom.

And now this concept of promotion kicks in--

--and reorganizes us electronically as follows.

According to our discussion, we need three equivalent orbitals down here with the three electrons in to pair up with the three electrons that come into the problem from the three hydrogen atoms.

At the end we will show how those electrons from the hydrogen atoms come in and pair up with these three electrons on a promoted boron atom. Up here we have the boron 2pz orbital. That stays by itself. And down here we are going to have a set of sp<sup>2</sup> hybrids.

The idea is now somehow we are going to get three orbitals down here by mixing one part S and two parts P. And, if we do this correctly mathematically, these will have the right orientation in space to be hybrids that have proper directionality for good overlap with our hydrogen 1s orbitals.

These are going to be three equivalent hybrids.

How do we do that? Well, we are going to get our equations for hybridization.

And we are going to develop these using some of the results from quantum mechanics, with is what Pauling did.

And essentially what we are going to do is seek equations that have one part  $s$  and two parts  $p$ , each of them, but which point in the correct directions in space for making three separate two electron bonds between the boron and the three hydrogens.

And so, I will just call them  $sp^2$  of A, because we are going to need one that points toward that A hydrogen which is along the positive  $x$ -axis, we are going to need one that points toward the B hydrogen and we are going to need one that points toward the C hydrogen. And the idea here is that we are going to have some amount of the boron  $2s$ ,  $p_x$  and  $p_y$ .

Because  $p_z$  is not contributing to these three hybrids. And each one of these is going to have some quantity of the three orbitals that we have available. And what you need to keep in mind here in setting up equations like this is that  $p_x$  has a definite spatial orientation with respect to the coordinate system that we have chosen.

And so does  $p_y$ . And the way that we will make this come out using our blue chalk is to note that we have a coefficient  $C_1$ ,  $C_2$  and  $C_3$ . Our job is going to be to find the values of these coefficients,  $C_4$ ,  $C_5$ ,  $C_6$ ,  $C_7$ ,  $C_8$  and  $C_9$ .

We can use the rules of quantum mechanics, and I am going to summarize a few of these rules for you before this lecture ends, to find the values of these constants. Let's go over here and begin.

Let's make note of the dictates of symmetry. I will reference symmetry a couple of times today in class in working on this problem of finding those coefficients one through nine. The neat thing is that the  $2s$  orbital centered on that boron, which is going to be participating in these hybrids that are going to point toward hydrogens A, B and C, that  $2s$  orbital is spherically symmetric. Its wavefunction is the same as you go radially out from the boron center in any direction into space.

What that symmetry consideration dictates is that there will be the same amount of boron  $2s$  in the hybrids for A, as for B, as for C. And what that means is that  $C_1$  is equal to  $C_4$  is equal to  $C_7$ .

And we are going to need a value for this. And we can get a value for that by taking into consideration something called unit orbital contribution.

What that says is that we have to use the boron's 2s orbital completely and identically once in that set of three equations. In other words, we are going to distribute it evenly among those three hybrids. And we have to distribute all of it evenly among those three hybrids. And here we are going to be interested in the square of the coefficients. And that is because when we talk about atomic orbitals we know that the probability of finding an electron in that orbital is related to the square of the wavefunction.

And so, normally when we plot orbitals, like I just did with the pi bond of ethylene a few minutes ago, we are making an isosurface that corresponds to some percent probability of finding the electron at that point in space. So, we are interested in probability distributions. And these are related to the square of the wavefunction. Here, for unit orbital, we are going to say that  $C_1^2$  equals  $C_4^2$ .

Sorry, plus  $C_4^2$  plus  $C_7^2$  is equal to one. And, therefore,  $C_1$  is equal to  $C_4$  is equal to  $C_7$  is equal to one over root three. Now we have found  $C_1$ ,  $C_4$  and  $C_7$ . And, if we are going to complete  $sp^2$  of A, get this first hybrid of the three, I am going to go across this way.

I just went down one, four and seven and pointed out that by the symmetry of the s orbital and due to the fact that the s orbital contributes once, unit orbital contribution, we could get  $C_1$ ,  $C_4$  and  $C_7$  equal to one over root three. Now I am interested in  $C_2$  and  $C_3$ , so let's draw a little picture.

This, remember, is our 1s orbital on HA. And what we are trying to do is to construct a hybrid focusing on that top equation that will be directed at HA. And we are keeping our axes the same as before so that x points up and y goes to the left, as I am drawing it here.

And z would be coming out at us. What I am going to draw now is a picture of the boron's 2p<sub>y</sub> orbital. And, as I usually do, I am taking the convention that the negative phase lobe of the boron's 2p<sub>y</sub> orbital-

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Negative is shaded. That is my convention. That 2p<sub>y</sub> orbital lies in the xy plane and points along y. Its positive lobe, in fact, points along

positive  $y$ . Its negative lobe points along negative  $y$ . And what can we say about the relationship of HA's orbital to the  $2p_y$  orbital of that central boron atom?

Let me phrase it this way. The  $2p_y$  orbital of our central boron atom has a nodal plane? What is that nodal plane?  $xz$  is a nodal plane of the  $2p_y$  orbital right here. Just like this. And so, what you see is that this HA is not only in the nodal plane of  $2p_z$ , it is also in the nodal plane of  $2p_y$ .

And that means any positive interference by bonding between HA's  $1s$  and the positive lobe of  $2p_y$  would be exactly canceled by the equal and opposite negative interference between a hydrogen's  $1s$  orbital and the negative phase lobe on  $2p_y$ . And that means that we know the value of  $C_3$ .

We can say, therefore,  $C_3$  is equal to zero. That is really cool because now we are going to be able to bring in one more consideration and complete the formula for  $sp^2$  of A.

We are going to be able to use the normalization condition--

--which tells us that  $C_1^2 + C_2^2 + C_3^2$  is equal to one.

Once we formed this new hybrid by mixing together S and P wave functions, we are going to find that this normalization condition must be satisfied for the hybrid orbital just as it is satisfied for these atomic orbitals. That is so that the probability of finding an electron somewhere in space associated with this hybrid wavefunction is one, if there is an electron in this orbital.

That is where this comes from. And we know that  $C_3^2$  is zero.  $C_1^2$  is one over root three. So, we know that  $sp^2$  of A is equal to one over root three. And then we can say that, by virtue of this and the fact that  $C_3$  is zero,  $C_2$  could be equal to either plus or minus the square root of two over three.

And we have to figure out which one of these to use. Remember that  $C_2$  is the coefficient on  $p_x$ . Let's reference our diagram on our coordinate system. We have our  $x$ -axis and our  $y$ -axis.

And we are looking for the sign of the coefficient on the boron  $2p_x$  orbital. That is our  $C_2$  coefficient. And I am shading negative here.



And, in order to overlap constructively and form a bond to the 1s orbital of HA, we want positive as our coefficient.

Because that is going to make the same phase lobes interact in a sigma fashion. We know that  $c_2^2$  of A is equal to one over root three times the boron's 2s orbital plus the square root of two over three 2px orbital.

And now that we have the coefficients on that hybrid orbital, we can draw a picture of what that is. That is equal to taking the boron 1s orbital here and adding to it the 2px orbital that looks like this. This is the conceptual breakthrough that Pauling made.

You could mix atomic orbital wavefunctions located on a central atom in order to generate these hybrids that have the proper directionality for good overlap with the peripheral atoms that bond to the central atom. And when I do this what you can see is that we are going to get constructive interference with the positive lobe and destructive interference with the negative lobe when we add this boron 2s orbital to the boron 2px orbital.

And that should give us something that looks like this, with an enlarged lobe pointing along positive x and a diminished negative node pointing along negative x. That is our hybrid. We have developed some coefficients here. We just got it pictorially, and here we show you the picture of the hybrid. And then we need to continue.

We need to use the remainder of our 2px orbital. One thing we cannot do in constructing a set of hybrid orbitals from a set of atomic orbitals is forget to use part of our orbital.

We need to use all of the orbital that we are given to construct these hybrids with. And what that means is we have now a relationship between  $c_5$  and  $c_8$ , because we now know  $c_2$  is plus root two over three. Let's use this orbital idea and reference to px.

And say that  $c_2^2$  plus  $c_5^2$  plus  $c_8^2$ , these are all the coefficients that deal with the px contributions to these three hybrids, is equal to one. And we know  $c_2^2$  is equal to two-thirds.

And now let's draw a picture to help us figure out something else about  $c_5$  and  $c_8$ . Here I am simply representing, with the same

coordinate system that I am using throughout, the boron atomic orbital that is the  $2p_x$  orbital.

And, if I consider down here the  $s$  orbitals on HA and HB, I can say something about the way in which  $2p_x$  interacts with HA as compared with the way in which it interacts with HB. Notice that these HA and HB atomic positions are mirror images of each other with respect to this  $2p_x$  orbital in the middle.

That tells us that  $C_5$  must be equal to  $C_8$ . We are using symmetry as a mathematical argument here to say that  $C_5$  is equal to  $C_8$ . Therefore, we can figure out exactly what  $C_5$  and  $C_8$  are because we already know that  $C_2$  squared is two-thirds.

We know that  $C_5$  squared plus  $C_8$  squared has got to be equal to one-third. And that means that  $C_5$  is equal to  $C_6$ , sorry,  $C_8$ , which is equal to one over the square root of six.

Because we put this in here, we will get a sixth plus a sixth, two-sixths, which is one-third plus the two-thirds, which will be one. And so, we know it is one over root six. However, it could be a positive or a negative. And we need to figure out just which it is. Is it positive or is it negative here? And I will come back to that issue just in a moment when we draw these functions.

But notice that these are the coefficients on  $2p_x$  and the positive lobe points up toward HA. We are going to need it to be flipped around and be pointing down if we are going to form bonds to HA and HB. So, that will dictate the sign here as negative one over root six. We do not have yet the complete equations for  $sp^2$  of B and  $sp^2$  of C because we need  $C_6$  and  $C_9$ .

Let's see how we can get those.

$C_6$  and  $C_9$  relate to the  $p_y$  orbital that is oriented like this with reference to our coordinate system with the negative phase shaded as follows. And specifically  $C_6$  relates to the interaction with this HB down here.

And  $C_9$  relates to the interaction with the  $1s$  orbital on HC down here on the lower right. And because this  $p_y$  orbital changes phase as we pass through the origin, and we want the positive phase to match up both with HB and with HC in the contributions to the hybrid

wavefunctions, we are going to know, and by the symmetry of this problem that these are negative mirror images of each other.

So, we know that  $C_6$  is equal to negative  $C_9$ . And if we put that together with unit orbital contribution we can see, because we know that we have our  $sp^2$  of B and  $sp^2$  of C, both of them have one over root three of the 2s contributing.

And then we are looking for six and nine. We found out over there that both of them have negative one over root six as the coefficient on  $p_x$ .

And then we know that since this is the one that points to B we do not need to flip the phase on  $p_y$  to get a bond forming between  $p_y$  and HB. This is going to be a positive and then this one is going to be a negative for the reasons I just mentioned that we are going to need to flip that  $p_y$  contribution to  $sp^2$  of C, as compared to  $sp^2$  of B in order to get this positive lobe over here interacting with HC in that function.

I am going to draw these functions in just a moment. But now, when we note that normalization requires that the sum of the squares of the coefficients B equal to one, and we know that  $C_3$  was zero so that there is no contribution at all of  $p_y$  to  $sp^2$  of A, and all of it must be here and here, that means that our coefficient is one over root two of  $p_y$ .

Using these restrictions from quantum mechanics, we actually have coefficients on the  $sp_x$  and  $p_y$  orbitals that show how they go together. And the way in which these add up is similar to what we have seen over here. It is a little more complicated because both  $p_x$  and  $p_y$  contribute.

Let me show you what they look like. This mathematical manipulation of these functions produces linear combinations that all three look the same as the symmetry of this problem would dictate. It is a three-fold symmetry type of problem. And this is our  $sp^2$  orbital pointing toward B with this mathematical form.

We have to flip around  $p_x$  so that the positive lobe of  $p_x$  contributes down here. We do not have to flip  $p_y$ . And we have different amounts of  $p_x$  and  $p_y$  in this hybrid wavefunction. But the math of the atomic orbitals guarantees that this form would be physically indistinguishable from this one over here.

They would look exactly identical if I plotted a probability density isosurface. These two-dimensional pictures that we draw on the board are like slices through three-dimensional probability density isosurfaces. That is what these representations are. And then we note that the  $p_y$  orbital is flipped around when we form  $sp^2$  of C.

And that leads to this appearance.

I would like to show you what one of these might look like if you calculated it from the math that we have developed here.

I have actually got more work to do here in the next five minutes, so let's keep our concentration. Look at this orbital.

This thing is a beautiful hybrid orbital. And I have calculated this with reference to a particular arbitrary molecule. This was calculated with reference to the water molecule. The positions of the nuclei in the water molecule are indicated by these arbitrary sized spheres. That is a typical ball and stick representation of a molecule in 3D. You can see that the oxygen of the water molecule is colored red in there. That is arbitrary. And then we have the hydrogens in white.

And then I have a big positive lobe in blue here and then a smaller yellow lobe that is our negative lobe on this orbital here, which is an admixture of an  $s$  orbital with a  $p$  orbital. I am not telling you the actual coefficients that went into this particular hybrid, but you can see how if I were to take a two-dimensional slice along the long axis of this hybrid orbital, it might look something like what we have drawn over there.

Namely with one nice large directed lobe that can have good overlap with a hydrogen  $1s$  orbital in order to give rise to a good two electron bond between hydrogen and boron. And let me illustrate how that impacts on how we draw our energy-level diagram for the  $BH_3$  molecule. What we have now is a situation in which, as you go up in energy, you find three orbitals that are all at the same energy.

These lines indicate places where we can put electrons. And, in fact, they look like this.

They represent positive interference up along  $x$ .

Positive interference between a  $sp^2$  hybrid that points down at atom B. Right here overlapping nicely with the hydrogen 1s wavefunction that is sitting out there surrounding that nucleus. And then over here is our hybrid orbital  $sp^2$  of C that points down here and interacts with the hydrogen 1s orbital on atom C.

And so, the idea is now this system,  $BH_3$ , has a total of six valence electrons. Valence shell electron pair repulsion theory could be used by you to predict the geometry that we started with for this problem. But now we can populate these bonding orbitals with electron pairs, as shown here. And then this problem has one more aspect to it, namely that up here somewhere higher in energy there is a 2p $_z$  orbital on the boron that is empty. And this empty orbital--

--is our feature that gives this molecule Lewis acid character. We know that this is an electron deficient system. It does not satisfy the octet rule.

And, specifically, where it is missing electrons are in that boron 2p $_z$  orbital. That allows you to predict something about the stereochemistry of reactions, for example. It says that if some nucleophile or Lewis base, a source of a pair of electrons is going to come in and approach that planar  $BH_3$  molecule, it will do so either along positive z or along negative z because that is where the big lobes are of that empty p $_z$  orbital point.

And this valence bond theory--

--satisfies this problem, that Pauling noticed, of how do we make three identical bonds in a plane that contains three dissimilar atomic orbital wavefunctions, an s orbital p $_x$  and a p $_y$ ?

Well, he found that mathematically you can mix them together in ways that gives you three identical hybrids that have the needed directionality for the forming of these three two electron bonds. There is an alternative solution to this problem, and we will call that molecular orbital theory. Don't forget about Robert S. Mulliken, MIT undergraduate thesis 1917. And MO theory is a different perspective on electronic structure theory for molecules.

And we will launch into that on Wednesday.